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NEW YORK UNIVERSITY

College of Engineering

RESEARCH DIVISION

University Heights, New York 53, N. Y.

DEVELOPMENT OF IMPROVED TITANIUM ORGANIC COMPOUNDS FOR USE AS HYDRAULIC FLUIDS

March 15, 1963

Prepared under Navy, Bureau of Naval Weapons
Contract NOw 62-0647-d

TECHNICAL REPORT NO. 4
Covering the period

November 16, 1962-February 28, 1963

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ABSTRACT

This Report No. 4 covers the fourth period of the project, but the duration of the project has been extended to June 30,1963 by letter of 24 January 1963(Ref:NPR-33-AWK/33). In this period two special modifications of the fluid tetraisopropyltitanate/basic zincoctoate reaction product have been developed with the aim to produce increased stability under the test requirements for a hydraulic fluid while maintaining the fire safety conditions, which are outlined in the preceding report.These products are modifications of the product with tetra butyl tin and a modification of the product with tri-isopropyl borate. Special attention has been given to the relationship between the diluted mixtures of these products, using inhibited silicone fluid 510 as diluent, and four-ball wear-test scar marks, and also to viscosity changes at low temperatures. The work is continuing.

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SUMMARY

This fourth report period of Contract NOw 62-0647-d is not a final report period, since the work on the contract has been extended to June 30, 1963.

During this period the work has continued the improvement of the fire safety of the product, as outlined in the Summary of Report No. 3. Also, special effort has been made to explore two new groups of complex fluids which appear to be especially promising for the aims of the project.

It has been pointed out throughout these reports that tetra alkyl titanates, such as the commercial tetra isopropyl titanate, inter-react with another group of metal organic products, such as basic zinc octoate or zinc 2-ethyl hexanoate (22% Zn), and that hereby fluid products are being formed of very desirable properties. It has also been pointed out, however, that in oxidation tests and in hydrolytic stability tests this complex fluid requires an additional stabilization by a further removal of any retained still-reactive group. The stabilization has been carried out by a redistillation with such organic fluids as benzyl alcohol. In SECTION II-D-3 of the present report some exploratory tests were made of a distillation of the initial product with alcohols containing a halogen group, such as chloroethanol. In the preceding project (Contract NOw 61-0434-d), the best results were obtained by reacting the initial product with a tetra alkyl silane, especially di-n-dodecyl di-n-octyl silane (Olin Mathieson), and the resulting modified complex had highly desirable properties, as reviewed in the Summary to Report No. 2 of the present project.

The difficulty here was in the fact that this di-di type silane is not commercially available, and its laboratory preparation is quite difficult. In SECTION II-A of the present report some experiments were made using a tri-one type silane, such as tri-n-decyl-octadecyl silane (Dow Corning). The results were interesting, however this silane is available only in very limited quantities commercially.

It was desirable, therefore, to find other metal organic modifying agents which are commercially available. In as much as the tetra alkyl titanates and the zinc octoate are commercially available, a commercially available modifying agent would contribute to make the products of this development accessable for further large-scale preparations. An interesting phenomenon of the modification made in the preceding project with tetra alkyl silanes, was that there was a silicone-carbon bond available, instead of the titanium-oxygen-carbon figuration of the tetra alkyltitanates. In reviewing other possible modifying agents containing metal-carbon bonds, it was observed that most of such metal-carbon bond fluids are readily combustible; the results with a modification using a tetra butyl tin, however, were satisfactory.

Another modification contained boron, but here the carbon radicals were bound to the boron by an OR-group. The material which was used here as modifying agent was tri isopropyl borate.

The preparation of these modifications are tabulated in SECTION II-B and SECTION II-C in PART II of this report.

It has been pointed out earlier that all these compounds have high flame points and have good stability in the various test groups; but that their viscosity is higher than desirable for their use at low temperatures and that they therefore require a viscosity reducing additive. As such a material cerium-octoate stabilized form of silicone fluid 510 (Dow Corning) had been developed.

It is a highly interesting fact that this silicone fluid is a very poor lubrican and that the four-ball wear-test at 60°C. with 20 kilogram load and at 30 minutes test length produces scars of 1 to 2 mm. length.

The product of of this project alone produces under the same conditions scar lengths of 0.3 and 0.35 mm.

In mixtures of these products with the stabilized silicone fluid as viscosity

reducer, a considerable amount of poor lubricating viscosity reducer can be added before the lubrication effect of the new product is being decreased to any practical extent. TABLES 153 and 154 show these results on the tetra butyl tin modified tetra isopropyl titanate/ zinc octoate reaction product and on the tri isopropyl borate modified material. Here a one-to-one mixture between such product with a stabilized silane showed nearly the same scar marks as the not diluted straight new product alone.

If the amount of diluent has been increased further; that means, if for instance 40 parts of one of the new products was viscosity reduced by mixing it with 60 parts stabilized silicone fluid, the scar lengths were increased, but still they were much smaller than the scars obtained from the silicone fluid itself. This indicates special lubricating properties of the new developments which are interesting enough to be studied further on.

These combinations of the new titanate derived complex fluids with inhibited silicone fluid as diluent are very interesting in respect to their viscosity/temperature relationship. TABLE 154 and FIGURE 1 show that a mixture of 40 parts of the tri isopropyl borate modified product with 60 parts inhibited silicone fluid, have a pour point of minus 85°F.; and at minus 45°F. and even below that the fluid mixture shows viscosities which appear to be well within the limits of pumpability.

It is interesting to note that the viscosity data of the same mixture produce a straight line relationship, when plotted on semi-logarithmic paper as viscosity versus the reciprocal absolute temperature in Fahrenheit.

In TABLE 155 and in FIGURE 2 the tin modified and the boron modified product are compared in 50:50 mixtures, 45/55 mixture and in 40/60 mixtures with the inhibited silicone fluid;and again the viscosity data are plotted on semi-logarithmic paper versus the reciprocals of the absolute temperature in Fahrenheit. Here the differences in viscosity at zero and at minus 45°F. connect, with the three mixtures of each of the two materials, in parallel straight lines, in spite of the fact that the change in viscosity and in pour point does not vary to the same extent upon increasing the ratio of dilution from 50:50 to 45:55 and to 40:60.

TABLE 153.

STUDIES ON THE TETRA BUTYL TIN MODIFICATION OF THE TETRA IBOPROPYL TITANATE / ZINC OCTOATE REACTION PRODUCT DILUTED WITH SILICONE FLUID 510 (AFTER INHIBITION WITH CERIUM OCTOATE)

MIXTURE OF 40 PARTS OF THIS PRODUCT WITH 60 PARTS OF INHIBITED SILICON FLUID 510

I. FOUR-BALL WEAR-TESTS MADE AT THE ESSO RESEARCH (ENJAY) LABORATORIES IN LINDEN, NEW JERSEY WITH A PRECISION SCIENTIFIC FOUR BALL WEAR TESTER (WITH FRIENDLY COOPERATION OF Mr. M.R. ROUX) 60°C./30 min/20 kg/ 600 RPM

THE TIN MODIFICATION UNDILUTED BALLS .....0.31 mm.
0.31 mm.
0.31 mm.
AVERAGE ...0.31 mm.

MIXTURE : 1 :1 (510) ..... BALLS .....0.25 mm.
0.30 mm.
0.30 mm.
AVERAGE ABOUT 0.3 mm

MIXTURE 40 PRODUCT : 60 (510) .... BALLS .... 0.43 mm.
0.40 mm.
0.42 mm.
AVERAGE ... 0.42 mm.

II. FOUR-BALL WEAR-TEST WITH TWICE THE LOAD ,THAT IS 4 0 Kg. (ON OUR INSTRUMENT) AT 70°C.

SCAR MEASURED UNITS .. 4.1
4.4
3.8
AVERAGE 4.1x FACTOR 0.145
or 0.594 mm.

III. VISCOSITY / TEMPERATURE

TEMPERATURE F	READING	FACTOR	CENTIPOISES	°R	COMPARE WITH BORATE MODIFICATION CENTIPOISES
60°	8.6	20	172 cps.	520	
40°	11.5	20	230 cps.	500	300 cps.
20°	25.0	20	500 cps.	480	450 cps.
0°	28.0	25	700 cps.	460	740 cps.

TABLE 154.

TEST DATA ON THE TRI ISOPROPYL BORATE MODIFICATION OF THE TETRA ISOPROPYL TITANATE / ZINC OCTOATE REACTION PRODUCT T 40 - 131

I. P O U R P O I N T S OF THE MATERIAL AFTER REDUCING THE VISCOSITY WITH CERIUM OCTOATE INHIBITED DOW SILICONE FLUID 510:

RATIO : 1 : 1 (510) ..... MINUS 61° F.

44.4 : 55.5% (510) ..... MINUS 65° F.

40 : 60 (510) ..... M I N U S 85° F.

II. F O U R B A L L W E A R T E S T S MADE ON THE PRECISION SCIENTIFIC - SHELL FOUR-BALL WEAR-TESTER IN THE SUMMIT LABORATORY OF THE CELANESE CORP. (WITH FRIENDLY COOPERATION OF Mr. JOHN KOCH AND PAUL SCHUMACHER)

TESTED AT 60°C ..... 30 min ---- 20 kg. - 600 RPM.

THE PRODUCT T 40-131 UNDILUTED : BALL 0.32 mm.
0.30 mm.
0.31 mm.
AVERAGE ..... 0.31 mm.

THE DILUTED PRODUCT 1:1 (510) BALL 0.37 mm.
0.38 mm.
0.36 mm.
AVERAGE ..... 0.37 mm.

THE DILUTED PRODUCT 40 : 60(510) BALL 0.42 mm.
0.47 mm.
0.49 mm.
AVERAGE ..... 0.46 mm.

III. V I S C O S I T Y OF THE MIXTURE OF 40 parts PRODUCTS AND 60 parts SILICONE 510

TEMPERATURE	READING	FACTOR	CENTIPOISES	T° R	1/ T°R x 100
77° F.	7.5	20	150	537	0.1865
65°	8.3	20	166	525	0.1905
50°	10.5	20	210	510	0.1960
40°	15.0	20	300	500	0.2000
20°	22.5	20	450	480	0.208
0°	37.0	20	740	460	0.217
- 20°	64.0	20	1280	440	0.227
- 45°	23.0	100	2300	415	0.241
- 65°	42.0	100	4200	395	0.253
- 75	65.0	100	6500	385	0.260

POUR POINT ....BELOW - 85° F.

(Plotted in FIGURE 1.)

T°R IS FAHRENHEIT ABSOLUTE or RANKINE
°R IS °F PLUS 459.58

FIGURE 1.

THE TRIISOPROPYL BORATE MODIFICATION OF THE TETRAISOPROPYL TITANATE/ZINC OCTOATE REACTION PRODUCT (T 40-131).

VISCOSITY REDUCED WITH CERIUM OCTOATE STABILIZED SILICONE FLUID 510.
(40 PRODUCT T 40-131
60 STABILIZED SILICONE FLUID 510.)

(PLOTTED ON SEMI-LOGARITHMIC PAPER - 3 CYCLES x 10 to the inch.)

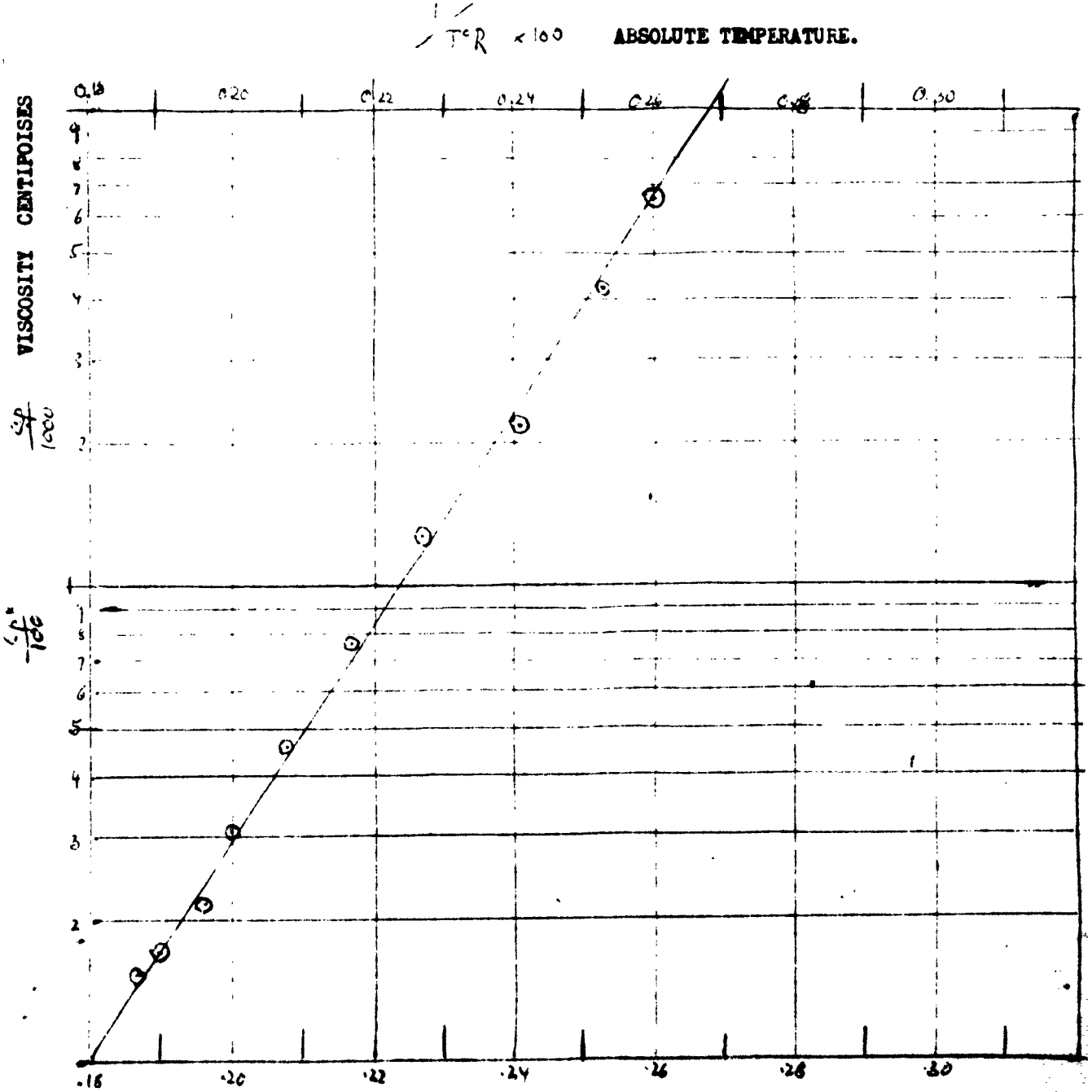


TABLE 155.

DATA OF THE TETRA BUTYL TIN MODIFICATION

AND THE TRI ISOPROPYL BORATE MODIFICATION

OF THE REACTION PRODUCT BETWEEN TETRA ISOPROPYL TITANATE AND ZINCOCTOATE

DILUTED WITH CERIUM OCTOATE INHIBITED SILICONE FLUID 510

THE TETRA BUTYL T I N MODIFICATION

MIXTURE : SILICONE FLUID	50	55	60
MODIFIED PRODUCT :	50	45	40
FOUR BALL WEAR TEST SCAR :	0.30 mm.		0.42 mm.
THE PRODUCT WITHOUT FLUID: 0.31 mm. SILICONE FLUID ALONE : 1.75 mm.			
POUR POINT	- 60°F.	- 65°F.	- 86°F.
VISCOSITY IN CENTIPOISES			
AT ZERO °F.	1900	1150	780
AT MINUS 45°F.	5350	3650	2450

THE TRI ISOPROPYL BORATE MODIFICATION

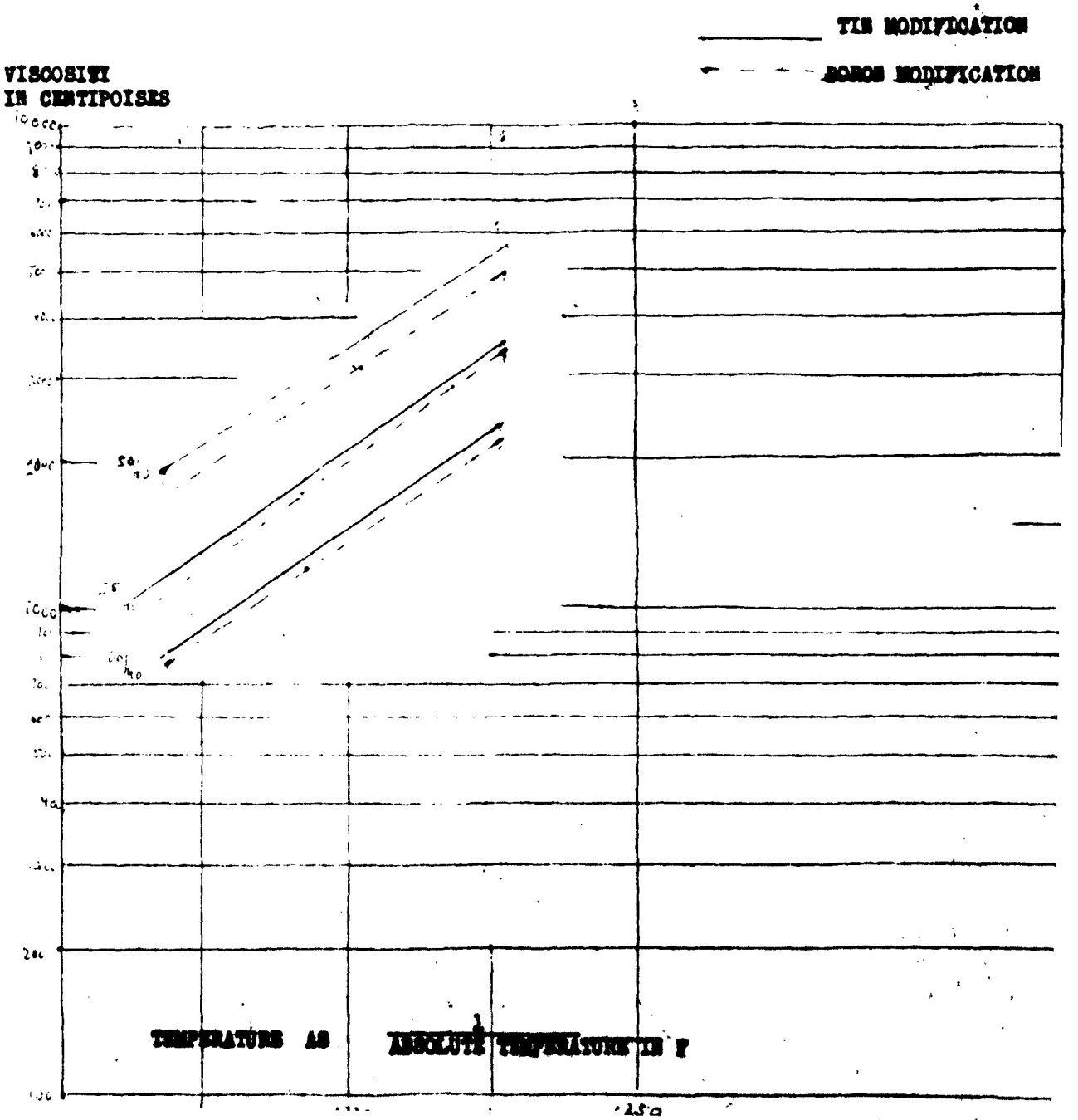
FOUR BALL WEAR TEST SCAR	0.37 mm.		0.46 mm.
THE PRODUCT WITHOUT FLUID : 0.31 mm.			
POUR POINT	- 61°F.	- 67°F.	- 88°F.
VISCOSITY IN CENTIPOISES			
AT ZERO F.	1700 cps.	1050 cps.	750 cps.
AT MINUS 45°F.	5000 cps.	3450 cps.	2300 cps.

THE VISCOSITY DATA ARE PLOTTED IN FIGURE 2.

FIGURE 2.

THE VISCOSITY OF THE MIXTURES OF THE TETRA BUTYL TIN MODIFICATION OR OF THE TRI ISOPROPYL BORATE MODIFICATION OF THE REACTION PRODUCT BETWEEN TETRA ISO-PROPYL TITANATE AND ZINC OCTOATE (22% Zn) WITH CERIUM OCTOATE-STABILIZED SILICONE FLUID 510.

TEST DATA TAKEN AT ZERO F AND AT MINUS 45 F AND PLOTTED ON SEMI-LOGARITHMIC PAPER (3 CYCLES x 10 TO THE INCH)



In further summarizing this report, the following aspects are listed:

PART I studies various applications of catalytic additives to the inter-reaction between tetra alkyl titanates and basic zinc octoate. Herein:

SECTION I-A uses titanium tetra chloride as catalyst in TABLES 156 and 157.

SECTION I-B uses aluminum trichloride as catalyst and this is at this time the preferred preparation method. These preparations are shown in TABLES 158-166.

SECTION I-C uses an organic catalyst, the butylene oxide 12, as shown in TABLE 167.

SECTION I-D further discusses the various preparations with respect to their properties. (TABLES 168-172). These are discussed further in the Introduction to Section I.

PART II studies the various forms of modification of the products of PART I with other metal organics.

SECTION II-A uses a tri n decyl octadecyl silane (TABLE 173-174).

SECTION II-B studies the modification with dibutyl tin dichloride and with tetra butyl tin uses the product of SECTION I-A and I-B (TABLES 175-185).

SECTION II-C uses as modifying agent tri-n-butyl borate, using it with the product of SECTION I-A and SECTION I-B (TABLES 186-190).

SECTION II-D uses a number of organic modifying agents, including one containing chlorine and one containing bromine (TABLES 191-194).

PART III resumes the work of SECTION E of Report No. 3, on the introduction of phosphorus groups into titanate compounds. In this respect, tests with 2-ethyl hexyl phosphate (tri octyl phosphate) are continued in SECTION III-A (TABLES 195-201). Also are shown combinations of the aliphatic tri octyl phosphate with the aromatic tri cresyl phosphate (SECTION III-B) (TABLES 202-203).

In SECTION III-C (TABLES 204-206) two other organo phosphates are being studied, the tris-B-chlorethyl phosphate and the tri butoxyethyl phosphate.

In SECTION III-D (TABLES 207-208) additional studies are made with di 2 ethyl hexyl phosphoric acid, continuing Section E-3 of Report No. 3.

PART IV (TABLE 209) gives new studies on the inhibiting of the silicone fluid 510 and the weight losses which occur hereby.

The work scheduled for the new report period is listed on the last page of the report.

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The work reported herein has been performed in Research Building No. 3 of the Research Division, College of Engineering, New York University, under the direction of Dr. Max Kronstein. The following members of the research staff have participated in the work:

Edward I. Stiefel	Research Aide
Robert A. Sierra	Research Aide
Jeannette Grace Musco, B.S.	Research Aide
Michael R. Carroad, B.Ch.E.	Research Aide
William Kapfer, Ph.D.	Chemical Engineer
Marion W. Kronstein, A.B.	Assist. Research Scientist.

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PART I. THE PREPARATION OF THE FLUID REACTION PRODUCT BETWEEN TETRA ISOPROPYL TITANATE AND BASIC ZINC OCTOATE.

INTRODUCTION

The inter-reaction between tetra alkyl titanates and basic zinc octoate has been discussed in preceding reports . The reaction is being studied further here as a step in the development of new complexes which are being obtained by further modifying this reaction product. Hereby, a number of different catalysts are being used, and the observation is made that different catalysts result in different properties of the reaction products.

SECTION I- A. USING TITANIUM TETRA CHLORIDE AS CATALYST. (TABLES 156-157)

The use of titanium tetra chloride as catalyst has been described in earlier reports (Report No. 3,Sect. B). It is described again in TABLES 156-157: once in the production of the initial reaction product, and once in a benzyl alcohol modification of these products. TABLE 157-III here shows a greater amount of decomposition product in a 72 hour oxidation test (200°C. (392°F.) with 5 liter air per hr.) than the product produced with aluminum chloride as catalyst.

SECTION I- B. USING ALUMINUM CHLORIDE AS CATALYST. (TABLES 158-166)

A considerable number of preparations have been made of the reaction product with aluminum chloride as catalyst. Special attention has been paid here to the observation that in the vacuum distillation there exists a very small cut of an organo distillate between the main low cut and the actual reaction product. When the few cc. of this yellow material is not separated, it causes a discoloration of the reaction product and a lowering of the flash point of the product.

Observations on the various preparations are given in the Tables. At the bottom of TABLE 159 is shown another study of the limited flammability of these products, which under proper preparation contain hardly any low cut, before reaching the flame point of the material itself, which is around and above 300°C. (572°F.).

(Continued on page 23.)

TABLE 156

PREPARATION OF THE TPT/ZINCOCTOATE PRODUCT WITH $TiCl_4$ AS CATALYST

I. T 43 - 30

USED 600 g. ZINC OCTOATE

200 g. TETRA ISOPROPYL TITANATE

3 - 4 drops $TiCl_4$

TIME min.	TEMPERATURE C.	F.	VARIACS TAPE	TOP	BOTTOM	HEAT DEVELOPED ON MIXING PRESSURE mm.	VOLUME ml.	REMARKS
-	40	(104°F)	15	40	45	5	-	
20	46		15	45	45	5	-	
55	75	(167°F)	15	45	45	5		CLEAR COLORLESS
70	100		15	45	45	5		CUT COMING
90	125	(257°F)	20	45	50	5		
110	140	(284°F)	20	45	50	5	150 ml.	
125	130		20	45	50	5	210 ml.	CUT I
150	145	(293°F)	25	60	65	8	-	FUMES
175	250	(482°F)	25	60	65	7		
195	315	(599°)	30	60	70	7	ABOUT 250 ml.	PRODUCT

II. T 43 -31

USED .... 570 g. ZINC OCTOATE

190 g TETRA ISOPROPYL TITANATE

3-4 drops $TiCl_4$

HEAT DEVELOPED ON MIXING

TIME min.	TEMPERATURE C.	F.	VARIAC	PRESSURE mm.	VOLUME ml.	REMARKS
-	30	(86°F)	40	5	-	
15	60	(140°F)	40	5	10 ml.	CUT I CLEAR COLORLESS
30	45		45	5	-	
60	45		45	5	-	
100	50		45	5	-	
110	35		45	5		
130	105	(221°F)	55	5	25 ml.	CLEAR COLORLESS
145	115	(239°F)	55	5	75 ml.	
155	130	(266°F)	55	5	120 ml.	
185	110	(230°F)	55	8	200 ml.	
						CUT II .... 212 g.
250	320	(608°F)	65	2		
280	320		65	2		PRODUCT OBTAINED .... 462 g.

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TABLE 157.

THE BENZYLALCOHOL MODIFICATION OF THE TETRAISOPROPYL TITANATE-ZINC OCTOATE REACTION PRODUCT WITH $TiCl_4$ CATALYST

I. REDISTILLATION OF THE REACTION PRODUCT (T 40 - 108)

TIME min.	TEMPERATURE C.	VARIAC	PRESSURE mm.	VOLUME ml.	REMARKS
-	27 (80°F)	70	0.5	-	
100	260 (500°F)	70	0.5		VAPOURS APPEAR
120	295 (563°F)	70	0.5	10	CLEAR ORANGE MATERIAL DISTILLS
140	295	70	0.5	40	
180	295	70	0.5	100	
220	310(590°)	70	0.5	200 ml.	NO MORE FLUID LEFT IN FLASK; VERY SLIGHT AMOUNT OF DECOMPOSITION.

II. BENZYLALCOHOL MODIFICATION OF THE PRODUCT I.

USED 185 PRODUCT OF I (T 40-108) T 40-109

55 g. BENZYLALCOHOL

-	28 (82°F)	70	2.3	-	
30	80 (176°F)	70	2.3		CLEAR COLORLESS, THEN LIGHT YELLOW FLUID DISTILLS
70	80- 95	70	2.3	70 ml.	
					65 g. LOW CUT
150	260 (500°F)	70	2.3		PRODUCT APPEARS
170	310(590°F)	70	2.3	60 ml.	GOLDEN YELLOW PRODUCT DISTILLS AT CONSTANT TEMPERATURE
200	312(593°F)	70	2.3	170 ml.	

III. O X I D A T I O N T E S T OF THE PRODUCT OF II.

USED 1 part OF PRODUCT II WITH

1 part INHIBITED DOW FLUID 510

FIRST WASHED WITH BENZENE AND ACETONE, HEATED TO ABOUT 200°C. UNDER 0.5 mm VACUUM

OXIDATION TEST AT 200°C . WITH 5 LITER / HOUR AIR PASSING

USED 50 g.. THIS PRODUCT MADE WITH $TiCl_4$ SHOWED AGAIN SOME DECOMPOSITION

THE PRODUCT MADE WITH $AlCl_3$ PASSES THIS TEST MUCH EASIER.

PART I- SECTION I-B.

TABLE 158.

REACTING TETRA ISOPROPYL TITANATE AND ZINC OCTOATE

WITH $AlCl_3$ AS CATALYST

I. T 43 - 46

USED .... 450 g.ZINC OCTOATE

150 g.TETRA ISOPROPYL TITANATE

SMALL AMOUNT OF $AlCl_3$

TIME min.	TEMPERATURE C.	VARIAC	PRESSURE mm.	VOLUME ml.	REMARKS
-	30 (86°F)	40	2-6	-	
15	52	45	2-6	10	LIGHT YELLOW
40	57 (135°F)	45	2-6	10	
60	100	45	2-6	35	
85	160 (320°F)	45	2-6	95	
105	175 (347°F)	45	2-6	145	
					CUT I
140	170 (338°F)	45	2-6	5	ORANGE FLUID
					CUT II
180	320 - 330 (608°F.- 626°F)	60	2-6	225 g.PRODUCT	

II. T 43 -47

REPEAT TEST WITH THE SAME QUANTITIES

-	30 (86°F)	40	2-6	-	
30	70	40	2-6	-	
35	110 (230°F)	40	2-6		LIGHT YELLOW CLEAR CUT COMES
70	160 (320°F)	40	2-6	55	
75	160	40	2-6	70	SLIGHT FUMES
85	160	40	2-6	95	
120	140 (284°F)	40	2-6	175	
140	130 (266°F)	40	2-6	185	
					CUT I
165	140	60	2-6	5	DARK ORANGE
					CUT II
190	327 - 333 (620°F)-(631°F)	60	2-6	400 ml. PRODUCT	

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TABLE 159

NEW PREPARATIONS OF THE REACTION PRODUCT BETWEEN

TETRA ISOPROPYL TITANATE AND BASIC ZINC OCTOATE (ZINC -2 ETHYL/-HEXANOATE) 22% Zn)

WITH $AlCl_3$ AS CATALYST (T 39 - 33)

USED.... 570 g. ZINC OCTOATE

190 g .TETRA ISOPROPYL TITANATE

0. 10 g Al Cl3

HEAT EVOLVED ON MIXING

TIME min.	TEMPERATURE C.	VARIAC	PRESSURE mm.	VOLUME ml.	REMARKS
15	58 (136°F)	50	2-4	10	CLEAR LIQUID C U T I
30	40	50	2-4	-	
45	62	50	2-4	-	
60	95 (203°F)	50	2-4	30	SLIGHTLY PALE LIQUID
65	102 (215°F)	50 - 55	2-4	50	PALE LIQUID
75	105	55	2-4	80	PALE YELLOW LIQUID
90	125 (257°F)	55	2-4	145	PALE YELLOW LIQUID
105	125	55	2-4	195	
130	85	55	2-4	210	
155	110 (230°F)	55	2-4	210	
180	98	60	2-4	213.5 ml.	LIGHT BROWN C U T II
210	200 (392°F)	60	2-4	-	
230	230 (446°F)	65	2-4	-	
255	295 (563°F)	65	2-4	-	
315	320 (608°F)	70	2-4		PRODUCT IS COMING OVER
375	3 2 2 (611°F)	70	2-4		DISTILLATION OF THE VISCOUS YELLOW REACTION PRODUCT COMPLETED.

YIELD ..... 4 5 0 g.

STUDY OF THIS REACTION YIELD ON INFLAMMABILITY (T 39 - 34)

WHEN FIRST HEATED IN OPEN DISH TO 2 0 0 °C. (392°F) AND HOT BUNSEN BURNER FLAME WAS HELD AGAINST THE SURFACE, IT TOOK 6 0 SECONDS UNTIL A FLAME OCCURRED

WHEN FIRST HEATED IN OPEN DISH TO 2 2 5 °C. (437°F.) THE HOT FLAME PRODUCED A FLAME AFTER 2 6 SECONDS AND THE TEMPERATURE OF THE FLUID REACHED HEREBY 254 °C. (482°F) 489°F)

WHEN FIRST HEATED IN OPEN DISH TO 2 5 0 °C THE FLAME OCCURRED UNDER THE SAME TEST CONDITION AFTER 15 SECOND AND THE TEMPERATURE ROSE TO 260 °C (500°F)

(527°F) WHEN FIRST HEATED TO 275 °C. THE FLAME OCCURRED AFTER 3 SECONDS. END TEMP.: 275°C.

(572°F) WHEN FIRST HEATED TO 300 °C. THE FLAME OCCURRED QUICKLY. END TEMPERATURE : 300°C.

TABLE 160.

NEW PREPARATIONS OF THE REACTION PRODUCT BETWEEN TETRA ISOPROPYL TITANATE AND BASIC ZINC OCTOATE WITH $Al Cl_3$ CATALYST (II.)

T 39 - 35

USED : 450 g. ZINC OCTOATE 22% Zn

150 g. TETRA ISOPROPYL TITANATE

0.10 g. $Al Cl_3$

HEAT EVOLVED ON MIXING

TIME min.	TEMPERATURE C.	F.	VARIAC	PRESSURE mm.	VOLUME ml.	REMARKS
-	60	(140°F)	40	2-4	-	
15	60		40	2-4	10	CLEAR LIQUID
30	40		45	2-4	11	BEGINS TO SHOW PALE YELLOW
60	30		50	2-4	12	CUT
						C U T I
90	115	(239°F)	50	2-4	75	
105	105	(221°F)	50	2-4	90	
125	126	(258°F)	55	2-4	100	PURE YELLOW LIQUID
150	112	(233°F)	55	2-4	110	" " "
180	90		60	2-4	118	" " "
195	115		60	2-4	120	" " "
210	170	(338°F)	65	2-4	122	" " "
225	230	(446°F)	66	2-4	127	" " "
240	280	(536°F)	68	2-4	131	
250	290	(554°F)	70	2-4	136	
						C U T II
300	330	(626°)	70	2-4	150 g.	CLEAR VISCOUS REACTION PRODUCT
						C U T III

REPEAT TEST T 39 - 39
USING SAME AMOUNTS OF MIXTURE

-	18	(64°F)	40	2	-	
15	19		45	2	2	CLEAR LIQUID
45	30		60	2	2	CUT I NOT SEPARATED
55	98	(208°F)	55	2	62	PALE YELLOW LOW VISCOUS
60	98		55	2	77	" " " "
65	99		55	2	87	" " " "
135	44		60	2	170	CLEAR YELLOW LOW VISCOUS
150	110	(230°F)	60	2	171	LIGHT BROWN MORE VISCOUS
165	130	(266°F)	68	2	173	" " " "
180	245	(473°F)	68	2	175	" " " "
195	315	(599°F)	70	2	-	END OF LOW CUT, PRODUCT COMING
						C U T I/II
210	315		70	2		PRODUCT COMING
225	315		70	2		CLEAR YELLOW VISCOUS PRODUCT
240	312		70	2		STILL COMING OVER
255	315		70	2		STILL COMING OVER
270	316		70	2		STILL COMING OVER
300	316		70	2		STILL COMING OVER
315	320	(608°)	70	2		STILL COMING OVER
330	-		-	-		TOTAL YIELD ..... 300 g. (OBTAINED IN NARROW DISTILLATION RANGE IN SLOW DISTILLATION)

TABLE 161.

NEW PREPARATIONS OF THE TETRAISOPROPYL TITANATE/ZINC OCTOATE PRODUCT (III)

A. T 39- 36 : USED 450 g. ZINCOCTOATE 22% Zn

150 g. TETRA ISOPROPYL TITANATE

0.10 g. $AlCl_3$ HEAT EVOLVED ON MIXING

TIME min.	TEMPERATURE C.	F.	VARIAC	PRESSURE mm.	VOLUME ml.	REMARKS
15	40	(104°F)	40	2-4	7	CLEAR FLUID NOT VISCOUS CUT I
45	128	(262°F)	45	2-4	85	PALE YELLOW NOT VISCOUS
60	130		45	2-4	150	PURE YELLOW
85	120		50	2-4	167	PURE YELLOW
105	138	(280°F)	55	2-4	170	BROWN LIQUID NOT VISCOUS
120	285	(545°F)	55	2-4	171	BROWN LIQUID
135	318	(604°F)	60	2-4	174	END OF CUT II, PRODUCT COMING
						C U T II
155	315	(599°F)	53	2-4		PRODUCT COMING OVER
245	325	(617°F)	60	2-4		265 g. YIELD: CLOUDY, WILL BE REDISTIL -LED

B. T 39- 37 SAME AMOUNTS USED AS IN A

10	36		25	2-4	4	
20	33		40	2-4		CLEAR FLUID CUT I
35	45		45	2-4	-	
50	112		35	2-4	54	PALE ALMOST CLEAR LIQUID
70	115		35	2-4	109	" " " "
90	98		35	2-4	184	BROWN YELLOW LIQUID
155	65		40	2-4	199	" " "
180	130		50	2-4	201	" " "
205	285	(545°F)	55	2-4	201	END OF LOW CUT, PRODUCT COMING
						C U T II
210	310	(590°F)	55	2-4		PRODUCT COMING OVER
240	240	(464°F)	53	2-4		SOME VIGOROUS BUMPING
255	306	(582°F)	53	2-4		PRODUCT COMING OVER
270	310		50	2-4		PRODUCT COMING OVER
285	305	(581°F)	53	2-4		PRODUCT COMING OVER
300	309		53	2-4		PRODUCT COMING OVER
315	255	(491°F)	55	2-4		SOME BUMPING
345	-		-			YIELD ..... 150 g.

FLASK RESIDUE CREAMY COLORED

C) R E D I S T I L L A T I O N OF YIELD FROM A AND FROM B T 39 - 38

30	75	(167°F)	60	2	2	YELLOW LIQUID
40	98		60	2	15	" "
60	123		65	2	26	" "
70	190	(374°F)	65	2	29	LIGHT BROWN LIQUID
85	300	(572°F)	65	2	44	DARK BROWN AND VISCOUS
95	300		55	2	50	END OF REMOVED CUT
150	305	(581°F)	55	2	4	CLEAR YELLOW PRODUCT
210	305		55	2	5	
330	320	(608°F)	60	2	50	PURE CLEAR YELLOW PRODUCT
360	320		60	2	150	PURE CLEAR YELLOW PRODUCT
375	321	(610°F)	60	2	250 ml	PURE CLEAR YELLOW PRODUCT
390	322	(611°F)	60	2	300	PURE CLEAR YELLOW PRODUCT
420	320	(608°F)	60	2		

TOTAL YIELD .... 480 g. PRODUCT

TABLE 162.

MORE PREPARATIONS OF THE TETRA ISOPROPYL TITANATE -ZINC OCTOATE REACTION PRODUCT WITH $AlCl_3$ AS CATALYST

I. T 38- 107

USED... 300 g. TETRA ISOPROPYL TITANATE
900 g. BASIC ZINC OCTOATE
0.5 g. $AlCl_3$

TIME min.	TEMPERATURE C.	F.	I	VARIAC II	PRESSURE mm.	VOLUME ml.	REMARKS
-	30	(86°F)	50	30	2-4	-	
130	140	(294)	50	30		25	
160	145		50	30		125	
180	150	(302)	60	30		200	
200	160	(320)	70	30		290	
220	170	(338)	75	30		340	
230	220	(428)	80	35		360	LOW CUT
240	270	(518)	80	35	2-4	5	
260	280	(536)	80	35		10	
275	340	(644)	80	35	2-4	20	
280	340		80	35		20	
320	345		80	35		240	
330	335	(635)	80	35		340	
340	320	(608)	80	35		400	
360	318	(604)	80	35		550 ml.	PRODUCT

II. T 40 - 99

USED .... 266 g. TETRA ISOPROPYL TITANATE
800 g. BASIC ZINC OCTOATE
0.3 g. Al Cl_3

-	25	(77°)	60	60	2.5	-
35	105		60	60	2.5	LOW CUT APPEARS AS CLEAR COLORLESS
60	112		60	60	2.5	100 MATERIAL WHICH DARKENS FIRST TO
110	125		60	60	2.5	200 YELLOW, THEN TO ORANGE AS DISTILLA-
120	160	(320°)	60	60	2.5	250 TION PROGRESSES
160	185		60	60	2.5	275
180	150		60	60	2.5	278
						CUT I
200	195	(383°)	60	60	2.5	- CUT APPEARS
220	209	(408°)	60	60	2.5	5 RED LIQUID
						CUT II
240	285	(545°)	70	70	2.5	- PRODUCT APPEARS
260	298	(568°)	65	65	2.5	30
270	312		65	65	2.5	100 COMING AT CONSTANT TEMPERATURE
300	312	(593°)	65	65	2.5	300
320	312		65	65	2.5	500
340	315	(599°)	65	65	2.5	650 ml. YIELD ... 640 g.

LITTLE DECOMPOSITION MATERIAL IN FLASK

TABLE 163.

MORE PREPARATIONS OF THE REACTION PRODUCT OF TETRA ISOPROPYL TITANATE AND ZINC OCTOATE WITH $AlCl_3$ AS CATALYST

I. T 42 - 129

USED 900 g. ZINC OCTOATE 22%

300 g. TETRA ISOPROPYL TITANATE

0.3 g. $AlCl_3$ HEAT ON MIXING

TIME min.	TEMPERATURE C.	VARIAC	PRESSURE mm.	VOLUME ml.	REMARKS
-	25	40	10	-	
60	110	65	7	25	CLEAR, SLIGHTLY YELLOW
80	125	65	7	90	
100	135	65	10	160	
110	145	65	10	240	
120	130	65	10	320	
					C U T I
180	70	70	10	5	DARKER YELLOW
210	125	70	10	15	
270	220 (428°F)	75	10	25	
300	280 (536°F)	75	10	____	END OF C U T II.

PRODUCT CAME OVER BETWEEN 300 AND 315 °C ..... ABOUT 400 ml.
(572°F - 599°F)

II. T 42- 132

USED 450 g. ZINC OCTOATE 22 %

150 g. TETRA ISOPROPYL TITANATE

0.3 g. $Al Cl_3$ HEAT EVOLVED ON MIXING

-	25	45	2	-	
60	95	50	2	10	LIGHT CLEAR YELLOW
70	100	50	2	50	
110	110	50	2	100	
140	120	50	2	150	
180	130	50	2	165	CUT I
240	95	60	2	5	DARKER YELLOW
260	130	70	2	10	
300	240	75	2	15	CUT II
320	305 / 315 (581°F./ 599°F)	75	2	ABOUT	300 ml. PRODUCT

III. T 42-127 B E N Z Y L A L C O H O L M O D I F I C A T I O N OF PRODUCT

USED 150 g. BENZYLALCOHOL T O 300 g. PRODUCT (WITH $Al Cl_3$)

-	25	45	2-10	-	
30	95	45	2-10	10	CLEAR DISTILLATE
110	95	55	2-10	130	CUT I
170	170	60	2-10	30	YELLOW BUT CLEAR CUT II
190	250	60	2-10	10	DARKER MORE VISCOUS YELLOW
240	305 - 310 (581°F.- 590°F)	60	2-10	275 g. PRODUCT	

TABLE 164.

MORE PREPARATIONS OF THE REACTION PRODUCT BETWEEN TETRA ISOPROPYL TITANATE AND ZINC OCTOATE 22% Zn WITH $AlCl_3$ CATALYST

I. T 42- 134 USED ... 570 g.ZINC OCTOATE
190 g.TETRA ISOPROPYL TITANATE
0.5 g.$AlCl_3$

TIME min.	TEMPERATURE C.	VARIAC	PRESSURE mm.	VOLUME ml.	REMARKS
-	25	40	2	-	
30	40	45	2	15	CLEAR COLORLESS CUT I
60	60	50	2	-	
70	90	50	2	25	SLIGHTLY YELLOW
100	110	50	2	75	
130	115	50	2	150	
150	115	55	2	200	
200	150	70	2	220	DARKER YELLOW
260	280	70	1	225	
300	310 (590°F)	70	1		

PRODUCT CAME OVER AT 310°C.... ABOUT 600 ml.

II. T 42- 136 USED SAME AMOUNTS

-	25	40	2	-	
60	45	55	2	25	CLEAR AND COLORLESS CUT I
90	90	55	2	25	SLIGHTLY YELLOW
140	115	65	2	125	
240	265	70	2	220	
310	310 (590°F)	PRODUCT CAME OVER AT 310°C.... ABOUT 600 ml.			

III T 42- 140 USED 450 g.ZINC OCTOATE WITH 150 g TPT AND 0.5 g.$AlCl_3$

-	25	50	2	-	
30	40	50	2	25	CLEAR COLORLESS CUT I
90	110	50	2	65	SLIGHTLY YELLOW
120	130	55	2	135	
180	170	65	2	145	DARKER YELLOW
220	110	70	2	150	
280 / 350	AT 320 / 330	PRODUCT CAME OVER ..... ABOUT 300 ml.			

IV. T 42- 145
USED 525 g.ZINC OCTOATE WITH 175 g.TETRAISOPROPYL TITANATE (0.5 g $AlCl_3$)

30	27	55	3	10	CLEAR COLORLESS CUT I
60	95	60	2	45	SLIGHTLY YELLOW CLEAR
100	120	60	2	115	
140	120	60	2	195	
200	145	70	2	210	CUT II
220	160	70	2	10	DARKER YELLOW MATERIAL
280	270	70	2		CUT III
300	305	PRODUCT CAME OVER AT 310 / 320 C (590°F/608°) ..... 500 ml.			

TABLE 165.

MORE PREPARATIONS OF THE TETRAISOPROPYL TITANATE/ ZINCOCTOATE PRODUCT

I. T 40- 126

USED 1000 g . ZINC OCTOATE

333 g.TETRA ISOPROPYL TITANATE

0.4 g. Al Cl_3

TIME min.	VARIAC I	VARIAC II	PRESSURE mm.	TEMPERATURE C .	VOLUME ml.	REMARKS
-	60	60	1	30	-	
30	60	60	1	60		VAPOURS APPEAR
50	60	60	1	95		CLEAR COLORLESS FLUID APPEARS
80	60	60	1	100	30	
120	60	60	1	115	300	FLUID IS NOW YELLOW
135	60	60	1	125	350	
						END OF C U T I
150	60	60	1	70	-	TEMPERATURE RISE BEGINS
180	60	60	1	200		A REDDISH ORANGE FLUID APPEARS
					ABOUT 10 ml.	C U T II
220	60	60	1	295		PRODUCT APPEARS AND DISTILLS
280	60	60	1	295	400	AT CONSTANT TEMPERATURE
330	60	60	1	295 (563°F)	800	
						END OF DISTILLATON

II. T 40 - 128

USED 1200 g.ZINC OCTOATE
400 g.TETRA ISOPROPYL TITANATE
0.5 g. Al Cl_3

-	60	60	1	60	-	
60	60	60	1	90		VAPOURS APPEAR
70	60	60	1	98		CLEAR COLORLESS FLUID APPEARS
90	60	60	1	120	100	
110	60	60	1	140	200	FLUID NOW SLIGHTLY YELLOW
200	70	70	1	115	450	END OF CUT I WAS ORANGE
220	70	70	1	200	10	RED FLUID ..... CUT II
250	70	70	1	290		PRODUCT APPEARS
270	70	70	2	330	100	
330	70	70	2	330	300	CLEAR YELLOW PRODUCT
380	70	70	2	330 (626°F)	800	
				TOTAL YIELD	1900 ml.	

III. T 40 -129 USED 1000 g.ZINC OCTOATE
333 g.TETRA ISOPROPYL TITANATE AND 0.4 g Al Cl_3

-	60	60	1	60	-	
40	60	60	1	90		VAPOURS APPEAR
60	60	60	½	98	20	CLEAR COLORLESS FLUID
110	60	60	1	140	250	NOW YELLOWISH
130	60	60	1.5	150	350	END OF CUT I
220	60	60	1.5	200		DROPLETS OF REDDISH FLUID
300	60	60	1.5	310	150	CLEAR YELLOW FLUID PRODUCT
350	60	60	1.5	310	450	
400	60	60	1.5	310 (590°F)	900 ml.	PRODUCT

TABLE 166.

MORE PREPARATIONS OF THE TETRAISOPROPYL TITANATE/ZINCOCTOATE PRODUCT

I. T 40 -115

USED 1027 g. ZINCOCTOATE

342 g TETRA ISOPROPYL TITANATE

0.3 g $AlCl_3$

TIME min.	VARIAC I	VARIAC II	PRESSURE mm.	TEMPERATURE C.	VOLUME ml.	WEIGHT g.	REMARKS
-	70	70	1	30	-		
10	70	70	1	60	-		
20	70	70	1	90	-		CLEAR YELLOW FLUID APPEARS
30	70	70	1	95	50		
50	70	70	1	98	400		C U T I
70	70	70	1	50	-		
80	70	70	1	170			VAPOURS APPEAR
90	70	70	1	206	5		VISCOUS MATERIAL C U T II
110	70	70	1	290	-		PRODUCT COMING
130	70	70	1	310 (590°F)	50		CLEAR GOLDEN YELLOW DISTILLATE AT CONSTANT TEMPERAT.
210	70	70	1	310	800 ml.		YIELD ... 875 g.

USED FOR TETRA BUTYL TIN MODIFICATION

IN T 40-120

II. T 40 - 125

USED 900 g. ZINC OCTOATE

300 g. TETRA ISOPROPYL TITANATE

0.3 g. $AlCl_3$

-	50	50	1.5	30	-		
20	50	50	1.5	90			LOW CUT APPEARS
60	50	50	1.5	120	320		END OF LOW CUT
80	70	70	1.5	180	-		VAPOURS APPEAR
100	70	70	1.5	206 / 212 (402°F/413°F)			A SMALL CUT
130	70	70	1.5	280			PRODUCT APPEARS
200	70	70	1.5	312 /320 (593°F/608°F)			THE PRODUCT HAS COME OVER YIELD ..... 7 8 5 g.

(Continued from page 11.)

SECTION I - C. USING BUTYLENE OXIDE 12 AS CATALYST. (TABLE 167)

Butylene Oxide 12 has been used , in a new approach, instead of the metal chloride catalyst. The reaction product seemed first to retain a small amount of low cut material; but after its removal the flame point was at 320°C. (608°F.).

The material will be studied further.

SECTION I - D. STUDIES ON THE PREPARATIONS OF THIS SECTION I. (TABLES 168-172)

Different studies have been made in connection with the materials of this Section.

1. The low cut matter of the distillation between tetra isopropyl titanate and basic zinc octoate has been studied, reviewing especially whether or not this low cut might consist of unreacted tetra alkyl titanate. The method of study is described in TABLE 168. The result clearly indicates that this low cut does not consist of unreacted titanate.

2. TABLE 169 shows, in the upper part, an oxidation test of the reaction product between the alkyl titanate and the zinc octoate which had been prepared in the presence of water, as outlined in the preceding report (SECTION D). In the lower part of this table is given a comparative table of refractive indices for the various preparations of the reaction product. The products made with different catalysts differ at least in the last two numbers of the index.

3. TABLE 170 gives rubber swelling tests for the product made with $AlCl_3$ as catalyst, and for the 1:1 mixture of this product with non inhibited and with inhibited silicone fluid. The mixture with the inhibited fluid shows the least degree of rubber swelling (0.74%).

4. TABLES 171 and 172 tabulate the ratio between the density of the titanium and zinc bands in emission spectra of the product in various forms of preparation and of modification. Here the specimen made with $Al\ Cl_3$ as catalyst shows the strongest titanium line as compared to zinc. These differences in the intensity of the spectra

(Continued on page 28 .)

SECTION I - C.

TABLE 167.

USING B U T Y L E N E O X I D E 1 2 AS CATALYST

WITH TETRA ISOPROPYL TITANATE AND ZINC OCTOATE

I . T 42- 135

USING 125 g.TETRA ISOPROPYL TITANATE

375 g.ZINC OCTOATE

2 g. BUTYLENE OXIDE 12 HEAT DEVELOPED ON MIXING

TIME min.	TEMPERATURE C.	PRESSURE mm.	VARIAC	VOLUME ml.	REMARKS
-	25	2	50	-	
60	40	2	50	10	CLEAR COLORLESS C U T I
90	100	2	55	10	SLIGHTLY YELLOW CLEAR
120	125	2	55	50	
140	135	2	55	90	
160	100	2	55	120	
200	120	2	60	125	C U T II
220	200	2	70	15	DARKER AND MORE VISCOUS
260	265	2	70	___	C U T III
300	310	2	70	75	FIRST YIELD AT 310°C. (590°F)
			AGAIN	100 ml.	SECOND YIELD AT 310 C .

THE TWO PARTS DIFFER IN COLOR AND VISCOSITY.
FLASH POINT BEGAN AT 115 C .. BUT
FINAL FLAME POINT WAS NOT BEFORE 270 C . (518°F)

II. T 42- 138 REPEAT TEST USING 175 g.TETRA ISOPROPYL TITANATE
525 g.ZINC OCTOATE
2 g.BUTYLENE OXIDE 12 HEAT ON MIXING

-	25	2	45	-	
40	40	2	50	10	CLEAR AND COLORLESS
60	40	2	50	25	C U T I
95	95	2	50	25	LIGHT YELLOW
110	105	2	50	100	
	105	4	55	160	
	115	4	55	200	C U T II
	305	3	65		DARK AND VISCOUS MATERIAL COMING OVER
	310 / 320 (590°F./ 608°F)	3	70	300 ml.	PRODUCT

THIS PRODUCT SHOWS SOME FLASHING AT 130/ 135 °C, BUT AFTER A RETAINED LOW CUT HAS BEEN DRIVEN OFF BY HEATING TO 330 °C, (626 °F)

THE FLASH POINT IS AT 280 °C. (536 °F) AND

THE FLAME POINT ...AT 320 °C. (608 °F.)

REFRACTIVE INDEX OF PRODUCT (TEST I) (25.5 °C)..1.4549

SECTION I - D.

TABLE 168.

STUDY OF THE LOW CUT OF THE TPT/ZINCOCTOATE DISTILLATION

T 38 - 108/109

WHEN TO 44.7 g.TETRA ISOPROPYL TITANATE WATER IS ADDED CAUTIOUSLY BY BURETTE WHILE SHAKING AND ALLOWING THE HYDROUS TiO_2 TO SETTLE,THE ENDPOINT OF THE TITRATION IS ADJUSTED TO OCCUR WHEN THE DROP OF WATER NO LONGER FORMS ANY WHITE PRECIPITATION WITH THE CLEAR SUPERNATANT LIQUID.

THIS OCCURS WITH 10.7 g.WATER .

WHEN THE LOW CUT OF THE TPT/ZINCOCTOATE DISTILLATION IS COLLECTED BETWEEN 110°C.AND 134°C.AT 2 mm. PRESSURE,IT IS A YELLOWISH FLUID WHICH SMOKES (HYDROLYZES) SLIGHTLY WHEN EXPOSED TO THE AIR.

WHEN,TO 29.60 g.OF THIS FRACTION,WATER IS ADDED GRADUALLY UNTIL NO MORE WHITE PRECIPITATE APPEARS UNDER THE PROCEDURE DESCRIBED ABOVE, 4.50 ml. WATER ARE ADDED BEFORE THIS POINT IS REACHED.

ASSUMING THAT FOUR MOLS OF WATER ARE NECESSARY TO HYDROLYZE A $Ti(OR)_4$,THE EQUIVALENTS OF TITANATE CAN BE SEEN TO BE THE EQUIVALENT OF WATER (APPROX.WITH THE DENSITY 1) .

TITANATE USED ... 29.60 g. IF THIS FRACTION WOULD BE A $Ti(OR)_4$ IT WOULD MEAN THAT THESE $\frac{29.60}{\frac{Ti(OR)_4}{4}} = \frac{4.50}{\frac{H_2O}{1}}$ (4.50 ml.WATER COMPLETES THE HYDROLYSIS)

APPARENT MW. OF $Ti(OR)_4 = \frac{(29.60)(18)(4)}{(4.5)(1)}$ (This is qualitative rather than quantitative)

THE RESULTING M.W. WOULD HERE THEREFORE BE 474 AND THIS IS CLEALY NO TETRA ISOPROPYL TITANATE. IT THEREFORE MUST BE A REACTION PRODUCT ALREADY.

AFTER THE TITRATION WAS COMPLETED THE SUPERNATANT LIQUID WAS DECANTED (AFTER CENTRIFUGING) AND WASHED WITH WATER IN A SEPARATORY FUNNEL TO REMOVE ISOPROPYL-ALCOHOL WHICH MIGHT BE PRESENT) REFRACTIVE INDEX 26°C IS THEN 1.40945

TABLE 169.

OXIDATION TESTS

I. T 38 - 84

MIXTURE OF 30g INHIBITED DOW FLUID 510

30 g .TPT/ZINCOCTOATE PRODUCT MADE IN PRESENCE OF WATER AND MODIFIED WITH BENZYLALCOHOL

INITIAL WEIGHT .... 243.5 g.

FINAL WEIGHT ..... 226.5 g.

THE THREE METAL STRIPS :

ALUMINUM	INITIAL WEIGHT ...	0.4552 g.	AFTERWARDS	0.4554 g.	PLUS	0.0002g
COPPER	" " ...	0.4603 g.	"	0.4602 g.	-	0.0001g
STEEL	" "	1.2320 g.	"	1.2324 g.	PLUS	0.0004g

T 42- 137

REFRACTIVE INDEX TESTS AT 25.5°C

THE VARIOUS PREPARATIONS OF THE REACTION PRODUCT BETWEEN TETRA ISOPROPYL TITANATE AND ZINC OCTOATE

PRODUCT MADE WITH $TiCl_4$ CATALYST ,.....,,	1.4570
PRODUCT MADE WITH $AlCl_3$ CATALYST	1.4542
PRODUCT MADE IN PRESENCE OF WATER	1.4555
TETRA BUTYL TIN MODIFICATION OF PRODUCT MADE WITH $AlCl_3$ CATALYST	1.4576
PRODUCT MADE WITH BUTYLENE OXIDE 12 CUT I	1.4549
CUT II	1.4549

TABLE 170.

RUBBER SWELLING TESTS

I. T 43 - 38 TEST ON THE TETRA ISOPROPYL TITANATE / ZINC OCTOATE REACTION PRODUCT WITH Al Cl_3 AS CATALYST

SIZE OF RUBBER ..... 2 1/2 " x 1 "

WEIGHT OF RUBBER ..... 3.9822 g.

TYPE OF RUBBER .... NAVY SAMPLE # 1313 STD L 10/60 - 20/310

APPARENT WEIGHT UNDER WATER ..... 0.6026 g.

AFTER TEST ..... 0.6281 g. (AFTER 7 7 HRS AT 112°C. 233°F.)

PRODUCT USED ..... 80 g .

RUBBER SWELLING % ΔV ... $\frac{0.6281 - 0.6026}{0.6026}$ x 100 ..... 4.23 %

II. T 43 - 38 TEST ON A 1:1 MIXTURE OF THE SAME PRODUCT AND NOT INHIBITED (ORIGINAL) SILICONE FLUID DOW 510

SIZE OF RUBBER ..... 2 1/2 " x 1 "

WEIGHT OF RUBBER .... 4.0303 g.

APPARENT WEIGHT UNDER WATER ..... 0.6141 g.

AFTER TEST ..... 0.6433 g. AFTER 7 7 HRS AT 112°C. 223 F

RUBBER SWELLING % ΔV ... $\frac{0.0292}{0.6141}$ x 100 ..... 4.75 %

III.T T 43 - 40 TEST ON 1:1 MIXTURE OF THE SAME PRODUCT AND INHIBITED SILICONE FLUID DOW 510

SIZE OF RUBBER ..... 2 1/2"x 1 "

WEIGHT OF RUBBER .... 3.9917 g.

APPARENT WEIGHT IN WATER ..... 0.6341 g

AFTER TEST ..... 0.6388 g. AFTER 70 1/2 HRS. AT 115°C. 239°F.

RUBBER SWELLING % Δ V .... $\frac{0.0047}{0.6341}$ x 100 ..... 0.74 %

(Continued from Page 23.)

go parallel to the fact that the atomic weight of titanium is 47.9 as compared with the atomic weight of zinc which is 65.38. The difference is even greater in the atomic weights of boron, as introduced in the modification (10.82),and tin introduced in a modification (118.7). The band intensity, however, is not necessarily controlled by the atomic weight. This has to be studied further.

- - - -

TABLE 171.

STUDIES USING THE EMISSION SPECTRO ANALYSIS ON THE REACTION PRODUCTS.

I. INFLUENCE OF THE CATALYST ON THE REACTION BETWEEN TETRA ISOPROPYL TITANATE AND BASIC ZINC OCTOATE:

IN TWO TEST SPECIMENS OF THE REACTION PRODUCTS OBTAINED AROUND 300°C (572°F) IN THE VACUUM DISTILLATION.

ONCE ALUMINUM CHLORIDE WAS USED AS THE CATALYST

IN THE SECOND CASE AN ORGANIC CATALYST WAS USED, THE

1.2. BUTYLENE OXIDE

$CH_3 - CH_2 - C - H - CH_2 \; O$ (T 42-135)

THE REPORT OF THE SPECTRO CHEM LABORATORY IN FRANKLIN LAKES, N.J. STATES THAT THE SAMPLE PREPARED WITH ALUMINUM CHLORIDE HAS A HIGHER RATIO OF TITANIUM TO ZINC THAN THE MATERIAL PREPARED WITH THE ORGANIC CATALYST.

IN BOTH CASES THE ZINC LINES ARE CONSIDERABLY STRONGER THAN THE TITANIUM LINES. (IT IS TO BE CONSIDERED THAT TITANIUM HAS AN ATOMIC WEIGHT OF 47.9 AND ZINC OF 65.38).

BESIDES THE PRODUCT MADE WITH ALUMINUM CHLORIDE HAS A VERY FAINT ALUMINUM LINE.

II. COMPARED THE LOW CUT OF THE DISTILLATION OF TETRA ISOPROPYL TITANATE AND BASIC ZINC OCTOATE (WITH ALUMINUM CHLORIDE CATALYST) WITH THE FINAL PRODUCT, THAT MEANS THE CUT BETWEEN 110 (230°F) AND 134°C (273°F) (2 mm) WITH THE DISTILLATE CUT ABOVE 300°C (572°F) (2 mm), THE HIGH CUT HAS A MUCH STRONGER ZINC LINE THAN TITANIUM LINE.

THE LOW CUT HAS A NUMBER OF STRONG TITANIUM LINES, INDICATING A HIGH TITANIUM CONCENTRATION, AND HAS A LOW CONCENTRATION IN ZINC.

(IT SHOULD NOW BE STUDIED IF THIS ZINC IS PRESENT IN FORM OF A REACTION PRODUCT WITH THE TITANATE, OR IS IT DERIVED FROM A LOW CUT MATERIAL IN THE ZINC OCTOATE. THIS WILL BE PURSUED IN THE NEXT PERIOD).

TABLE 172

MORE EMISSION SPECTRAL ANALYSIS STUDIES REFERRING TO THE NEW MODIFICATIONS OF THE TPT/ZINCOCTOATE REACTION PRODUCT

III. IN TEST T 42-130 THE TETRA ISOPROPYL TITANATE/ ZINCOCTOATE REACTION PRODUCT HAD BEEN FURTHER REACTED WITH TETRA BUTYL TIN ,A $Sn R_4$ MATERIAL. IN TEST T 40 -124 THE TETRA ISOPROPYL TITANATE /ZINC OCTOATE REACTION PRODUCT HAD BEEN FURTHER REACTED WITH TRI-n- BUTYL BORATE, A $B(OR)_3$ MATERIAL.

THE TIN ORGANIC MODIFICATION SHOWS IN THE EMISSION SPECTRUM A NUMBER OF STRONG TIN LINES

THE BORON $(O R)_3$ MODIFICATION SHOWS ONLY WEAK BORON LINES.

TO EXPLAIN THIS IT MIGHT BE CONSIDERED THAT THE

ATOMIC WEIGHT OF TIN IS ..... 1 1 8 .7 AND THE

ATOMIC WEIGHT OF BORON IS .... 1 0 .8 2 .

THIS MIGHT INFLUENCE THE ACTUAL DIFFERENCE IN THE AMOUNT OF TIN OR BORON WHICH ENTERS THE COMPOUND. BUT THE ATOMIC WEIGHT ITSELF DOES NOT CONTROL THE DIFFERENCE IN THE DENSITY OF THE LINES BETWEEN TWO DIFFERENT ELEMENTS. THIS IS FURTHER TO BE STUDIED.

PART II. MODIFICATIONS OF THE PRODUCTS OF PART I WITH VARIOUS METAL ORGANIC FLUIDS.

INTRODUCTION

In earlier reports it has been pointed out that the reaction product of PART I still has at least one reactive position and that it is desirable for the requirements of the various tests, which are provided in the specifications for hydraulic fluids for airplanes, to substitute these still-reactive groups with stable groups. The modification of the product of PART I with benzyl alcohol was given as part of the tables in PART I. Here other modifications, or other introductions of new groups, are being discussed.

SECTION A. REACTING THE PRODUCTS OF PART I WITH A TETRA ALKYL SILANE. (TABLES 173-174)

At the end of the preceding project and in the first and second reports of the present project modifications with a certain tetra alkyl silane have been discussed . This can be classified as a Di-Di-type alkyl silane, as far as it contains two n dodecyl and two n octyl groups. This modification had been successful, but its production was difficult because it is difficult to introduce by Grignard reactions these two-times-two groups into the silanes. It would be easier to produce silanes which contain three groups of one kind and one of another kind. One of this type modification with a tri n decyl - octadecyl silane was carried out as shown in TABLE 173. Also, a modification with a diphenyl di dodecyl silane was carried out in TABLE 174.

The reactions were successful, but further studies indicated that these silanes also are only available to a very limited extent and that evidently their formulation would not be easy either.

SECTION B. REACTING THE PRODUCT OF PART I WITH TIN ORGANICS. TABLES 175-185).

It was therefore more desirable to use as modification agents metal organics which would be commercially available. In reviewing the metal organics which exist with metal carbon bonds and which at the same time are stable to a desirable degree, the tin organics have been selected for further studies as modifying agents for the product of PART I. First attempts were made to utilize the tin organics with tin-carbon bonds which would also contain one or two more easily replaceable halogen groups. That is

(Continued on page 34.)

TABLE 173.

REACTING THE TPT/ ZINC OCTOATE DISTILLATION PRODUCT WITH

TRI n DECYL-OCTADECYL SILANE (DOW)

T 40 -89

I. USING 50 g. TPT/ZINCOCTOATE PRODUCT T 40-84

AND 50 g. TRI n DECYL OCTADECYL SILANE

TIME min.	VARIAC	TEMPERATURE C.	PRESSURE mm.	VOLUME ml.	REMARKS
-	70	28	2.5	-	
70	70	195	2.5	-	VAPOURS APPEAR
80	70	210	2.5	5	ORANGE LIQUID
110	70	290	2.5	-	CLEAR LIGHT-ORANGE LIQUID APPEARS
120	70	305 (581°F)	2.5	5	CLEAR ORANGE FLUID DISTILLS AT CONSTANT TEMPERATURE
160	70	305	2.5	85	
165	70	309 (588°F)	2.5	88 ml.	CUT ENDS SOLID IN FLASK

II. OXIDATION TEST OF I. T 40 -91

TEST AT 200°C. WITH 5 LITER AIR PER HOUR
(392°F.)
AFTER THREE x 24 HOURS NO VISUAL SEDIMENT.

TRACE OF MICROSCOPIC SEDIMENT

VISCOSITY VERY GOOD. VERY LITTLE EFFECT ON METALS (COPPER AND STEEL REMAINED FAIRLY BRIGHT)

WEIGHT LOSS OF FLUID BEFORE TEST .... 50 g.

AFTER TEST ..... 45.5 LOSS 4.5 g..... 9 %

III. REPEAT PREPARATION TO I. USING 75 g. PRODUCT MADE WITH $AlCl_3$

T 40 -92 AND 75 g. C_{18} Si $(C_{10})_3$

-	70	28	2.5	-	
40	70	180	2.5	-	VAPOURS APPEAR
70	70	215	2.5	10	CLEAR ORANGE LIQUID
80	70	230	2.5	-	
90	70	280	2.5	-	
110	70	308	2.5	5	CLEAR LIGHT YELLOW LIQUID APPEARS
130	70	310	2.5	30	
150	70	310	2.5	80	
170	70	310	2.5	95	
180	70	315 (599°F)	2.5	99	CUT ENDS

TABLE 174.

MORE STUDIES ON REACTION PRODUCT BETWEEN THE TPT/ZINCOATOATE PRODUCT AND S I L A N E S

I. MORE ON THE PRODUCT MADE WITH T R I n D E C Y L -O C T A D E C Y L S I L A N E

P O U R P O I N T D A T A :

THE PRODUCT T 40- 92 (TABLE 173) ALONE ..... POUR POINT 0°F.

3 PARTS OF THIS PRODUCT WITH 1 PART INHIBITED

DOW FLUID 510 ..... POUR POINT - 10°F.

1 PART OF THE PRODUCT WITH 1 PART INHIBITED

DOW FLUID 510 ..... POUR POINT - 40°F.

1 PART OF THE PRODUCT WITH 2 PARTS INHIBITED

DOW FLUID 510 ..... POUR POINT - 70°F.

II REACTING THE TPT/ZINC OCTOATE PRODUCT WITH

DIPHENYL DI DODECYL SILANE (DOW)

USED 70 g.PRODUCT WITH Al Cl_3 CATALYST

70 g.DIPHENYL DI DODECYL SILANE

TIME min.	TEMPERATURE C.	PRESSURE mm.	VARIAC	VOLUME ml.	REMARKS
-	27	2.5	75	-	
50	150	2.5	75	-	SOME LOW CUT APPEARS
80	310	2.5	75	4	END OF CUT I
100	3 1 2	2.5	75	-	DISTILLATION PRODUCT APPEARS
160	312(593°F)	2.5	75	110	DROPWISE DISTILLATION OF A CLEAR ORANGE MATERIAL AT CONSTANT TEMPERATURE

III. O X I D A T I O N TEST OF THE PRODUCT OF II.

MATERIAL USED ..... 30 g TEST AT 200 C WITH 5 LITER AIR PER HOUR

MATERIAL AFTER TEST 29.6 g LOSS 0.4 g. or 1 . 1 % N O SEDIMENTATION

LITTLE VISCOSITY CHANGE LITTLE EFFECT ON METALS .

(Continued from page 31.)

why in TABLE 175 dibutyl tin dichloride is reacted with the product of PART I. In TABLE 176 the same material is used with a tetra alkyl titanate, and it was expected to further complex this reaction product with zinc octoate but the results were not satisfactory. Therefore new studies were made, starting with TABLE 177, in modifying the product of PART I with tetra butyl tin which is commercially available from the Anderson Chemical Division of Stauffer Chemical Company, in Weston, Michigan.

As the work on this modification continued, as shown in subsequent tables, a material was obtained which was uniform in its characteristics, and it passed the various tests successfully. Mixtures with inhibited silicone fluid 510 (Dow Corning) showed also good viscosity and good four-ball wear-test results and a good pour point. This work is tabulated in TABLES 178-185.

SECTION C. REACTING THE PRODUCT OF PART I WITH ORGANIC TRI BORATES. (TABLES 186-190).

The product of PART I was similarly reacted with tri-n-butyl borate and with tri isopropyl borate. The latter one was then pursued further, because the resulting modifications of the product of PART I had higher flash and flame points than with tri n butyl borate.

TABLES 187-190 give the various preparations and studies on the tri isopropyl modifications of the product of PART I. This material appears promising also and is under further evaluation.

SECTION D. INTRODUCING OTHER GROUPS IN THE COMPLEX MATTER OF PART I. (TABLES 191-194).

TABLE 191 shows a reaction of tri ethyl hexyl-tri melitate with tetra isopropyl titanate. This melitate is a commercially available material which is supposed to have good heat resistance and good stability under the required conditions of this development, but no desirable product has been obtained here.

TABLE 192 shows a replacement of the isopropyl groups of a tetra isopropyl titanate by benzyl groups followed by a complexing of the resulting tetra benzyl titanate with zinc octoate. A reaction product was obtained at a constant distillation range of 290°C (554°F) at 2-4 mm. pressure; but the yield was not high enough to warrant a greater

(Continued on page 54.)

SECTION II-B.

TABLE 175.

PRODUCT MODIFICATION WITH DIBUTYL TIN D I C H L O R I D E

I. PREPARATION OF THE PRODUCT : T 40-84

USED 300 g. ZINCOCTOATE AND 100 g. TETRA ISOPROPYL TITANATE WITH 0.2 g. Al Cl_3

TIME min.	PRESSURE mm.	VARIAC	TEMPERATURE C.	VOLUME ml.	REMARKS
-	3.5	50	27	-	
40	3.5	50	92	-	CLEAR YELLOW FLUID APPEARS
50	3.5	50	95	20	
70	3.5	50	110	90	
80	3.5	50	140	110	NO MORE FLUID APPEARS CUT I
90	3.5	60	85	-	
110	3.5	70	180		ORANGE LIQUID APPEARS
130	3.5	70	206	15	ORANGE LIQUID STOPS COMING CUT II
150	3.5	70	280	-	PRODUCT APPEARS
180	3.5	70	310	70	
220	3.5	70	320	180	
240	3.5	70	325 (617°F)	210	NO MORE PRODUCT COMES OVER WHITE MATTER IN FLASK.

II. REACTING THE PRODUCT OF I WITH DIBUTYL TIN DICHLORIDE : T 40-85

USED: 150 g. PRODUCT OF I
50 g. DIBUTYL TIN DICHLORIDE
THE MATERIALS WERE MIXED AND HEATED TOGETHER UNTIL THE DIBUTYL TIN DICHLORIDE HAD MELTED. THEN THE DISTILLATION WAS SET UP .

-	2.8	60	38	-	
30	2.8	60	170	-	CLEAR YELLOW FLUID APPEARS
40	2.8	60	170	20	NO MORE FLUID APPEARS CUT I
60	2.8	60	180	-	
80	2.8	60	250	-	
120	2.8	60	300	-	THERE SEEMS TO BE AN EXTENSIVE
150	2.8	60	330	5	DECOMPOSITION IN FLASK
170	2.8	60	350 (662°F)	-	
					INSPITE OF THIS SMALL AMOUNT OF PRODUCT HAVING STARTED TO COME OVER, THE FLASK CONTENT DECOMPOSED.

THE FLUID CUT I SOLIDIFIED ON STANDING OVER NIGHT.

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TABLE 176.

ATTEMPTS TO REACT DIBUTYL TIN DICHLORIDE WITH TETRA ISOPROPYL TITANATE

I. T 40-86 USING 142.5 g. TETRA ISOPROPYL TITANATE (1/2 mole)

150 g. DIBUTYL TIN DICHLORIDE

IN 50 g. ISOPROPANOL NO HEAT EVOLVED ON MIXING

TIME min.	VARIAC	PRESSURE mm.	TEMPERATURE C.	VOLUME ml.	REMARKS
-	40	2.5	35		ISOPROPANOL APPEARS
20	40	2.5	48	75 ml.	CUT I
40	60	2.5	95	-	CLEAR COLORLESS FLUID APPEARS
60	60	2.5	110	50	
80	60	2.5	115	100	FLUID TURNS YELLOW
110	60	2.5	120	150	NO MORE FLUID COMING CUT II
145	60	2.5	170	-	A CLEAR ORANGE FLUID APPEARS
170	60	2.5	175	60	
210	60	2.5	185	120	
230	60	2.5	180 (356°F)	140	FLASK CONTAINS ONLY 10 -20 ml.
					CUT III: DECOMPOSITION MATERIAL

IT APPEARS AS IF CUT II IS MOSTLY TETRA ISOPROPYL TITANATE AND CUT III DIBUTYL TIN DICHLORIDE, WHICH TURNS SOLID ON STANDING.

II. T 40-88 USING AN HYDROLYSIS OF THE CHLORIDE :

USING 71.2 g. TETRA ISOPROPYL TITANATE (1/4 mole)
75 g. HYDROLYZED DIBUTYL TIN DICHLORIDE

THIS WAS PREPARED AS FOLLOWS: FIRST IT WAS DETERMINED THAT THE DIBUTYLTIN DICHLORIDE IN WATER MAKES THE WATER ACIDIC (TESTED WITH pH PAPER). 75 g. DICHLORIDE WAS INTRODUCED INTO BOILING WATER AND BOILED FOR SEVERAL MINUTES. IT WAS THEN SEPARATED AND DRIED IN A DESICCATOR OVER P_2O_5 OVER-NIGHT. AFTERWARDS IT WAS MIXED AS INDICATED ABOVE. NO ALCOHOL WAS ADDED.

-	40	3.4	28	-	
50	40	2.8	98	-	CLEAR COLORLESS FLUID APPEARS
80	40	2.8	112	60 ml.	LIQUID TURNED DARKER YELLOW
100	40	2.8	80	70 ml.	TEMPERATURE REACHED 120 C, DROPPED
				CUT I	AGAIN AS DISTILLATION CEASED.
120	50	2.8	90	-	
140	50	2.8	168	-	VAPOURS APPEAR
143	50	2.8	174	-	CLEAR ORANGE LIQUID APPEARS
160	50	2.8	175	20	
180	50	2.8	180	50	
185	50	2.8	182 (359°F)	55	NO MORE FLUID COMING OVER CUT II

THE TWO CUTS APPEAR TO BE AGAIN THE TWO USED COMPONENTS.

TABLE 177.

MORE STUDIES BETWEEN TETRA ISOPROPYL TITANATE AND BUTYL TIN MATERIALS:

I. T 40-87

REACTING 71.2 g. TETRA ISOPROPYL TITANATE (1/4 moles)

WITH 86.6 g. TETRA BUTYL TIN (1/4 mole) NO HEAT EVOLVED ON MIXING

TIME min.	TEMPERATURE C.	VARIAC	PRESSURE mm.	VOLUME ml.	REMARKS
-	27	40	2.7	-	
50	100	40	2.9	-	CLEAR COLORLESS MATERIAL APPEARS
70	105	50	2.7	40	
80	115	50	2.7	75	CUT I ENDING
90	80	50	2.5	-	
100	60	50	2.5	-	
110	150	50	2.5	-	
120	173	50	2.5	-	CLEAR COLORLESS FLUID APPEARS
140	175	50	2.5	30	
180	188 (370°F)	50	2.5	80	CUT II ENDING

APPEARS AS IF THE TWO CUTS CORRESPOND WITH THE TWO INITIAL COMPONENTS.

II.T 40- 90

75 g. DIBUTYL TIN DICHLORIDE WERE DISSOLVED IN BOILING WATER AND K O H WAS ADDED UNTIL INDICATOR PAPER TURNS BASIC IN COLOR . THE RESULTING SOLIDS WERE WASHED WITH WATER UNTIL NEUTRAL IN EFFECT ON pH PAPER.

75 g. OF THIS SOLID WERE MIXED WITH
75 g. TETRA ISOPROPYL TITANATE (SLIGHT HEAT ON MIXING EVOLVED)

-	28	40	2.9	-	
30	90	40	2.7	-	VAPOURS APPEAR
40	99	50	2.6	3	CLEAR COLORLESS LIQUID
70	104	50	2.5	35	
80	110	50	2.5	45	
90	110	60	2,5	60	
100	115	60	2.5	62	END OF CUT I
120	80	60	2.5	-	
140	190	60	2.5	-	VAPOURS APPEAR
160	193	60	2.5	30	CLEAR ORANGE LIQUID
180	195 (383°F)	60	2.5	60	END OF CUT II SOLIDS IN FLASK

THE TEMPERATURE OF THIS HIGH CUT II IS HIGHER THAN THE TEMPERATURE WHEN THE DIBUTYL TIN DICHLORIDE DISTILLS. IT IS POSSIBLE THAT THE DIBUTYL TIN DICHLORIDE TURNED WITH KOH AT LEAST PARTIALLY INTO DIBUTYL TIN $-(OH)_2$ AND THAT THIS REACTS WITH Ti $(OR)_4$. MORE STUDIES ARE REQUIRED.

TABLE 178.

REACTING THE TPT/ZINCOCTOATE REACTION PRODUCT (MADE WITH $AlCl_3$ CATALYST) WITH TETRA BUTYL TIN ($(C_4H_9)_4Sn$

USED 180 g. TPT/ZINCOCTOATE REACTION PRODUCT ($AlCl_3$ CATALYST) AND

60 g. TETRA BUTYL TIN T-38- 103

FULLY SOLUBLE IN EACH OTHER FORMING A CLEAR GOLDEN COLORED SOLUTION.

TIME min.	TEMPERATURE C.	PRESSURE mm.	VARIAC	VOLUME ml.	REMARKS
-	28	2	40	-	
30	30	1	40	-	
60	35	1	50	-	
90	95	2	50	10	
95	95	1	55	25	COLORLESS DISTILLATE, SOMEWHAT SIMILAR ODOR AS PRODUCT
97	96	1	55	30	
					CUT I
109	130	1.5	60	10	
115	131	2	60	15	COLORLESS DROPWISE DISTILLATION
120	129	2	60	25	
130	128 (262°F)	2	60	30	
					CUT II
160	80	1	70	-	
180	50	1	70	-	MATERIAL IN FLASK GETTING DARKER
240	70	1	80	-	
280	120 (248°F)	1	80	-	
290	230	1	80	-	
300	285	1	80	5	
310	290	1	80	10	
330	290	1	80	30	
340	290	1	80	40	PRODUCT CLEAR YELLOW, SEEMS TO BE SOMEWHAT LESS VISCOUS
350	288	1	80	55	
360	270	1	80	55	
370	285	1	80	60	
375	280	1	80	90	
395	290	1	80	120	
406	290 (554°F)	1	80	130 ml.	

MIXTURE OF ONE PART OF THIS LAST CUT WITH

ONE PART INHIBITED DOW FLUID 510

HAS A POUR POINT OF MINUS 8 2°F .

TABLE 179.

MORE REACTIONS WITH TETRA BUTYL T I N

I. T 40 - 102 USED ... 200 g. TPT/ZINCOCTOATE PRODUCT WITH Al Cl_3 CATALYST(T40-99)

60 g. TETRA BUTYL TIN NO HEAT EVOLVED ON MIXING

TIME min.	VARIAC	PRESSURE mm.	TEMPERATURE C.	VOLUME ml.	REMARKS
-	60	2.9	25	-	
20	60	2.5	130		A CLEAR YELLOW FLUID DISTILLS
30	60	2.5	140	10	FLUID IS NOW COLORLESS
50	60	2.5	155	50	
70	60	2.5	170	80	
90	70	2.5	170 (338°F)	90	
					CUT I
115	80	2.5	320	-	PRODUCT APPEARS
140	80	2.5	320 (608°F)	60	

WHEN HERE SOME PRODUCT CAME OVER TOO FAST, IT WAS REDISTILLED AT 312°C. (593°F)

II. T 42- 130 USED .... 180 g. PRODUCT (WITH Al Cl_3 CATALYST)

60 g. TETRA n BUTYL TIN

MIXED WELL AND LEFT OVERNIGHT BEFORE DISTILLING

-	40	2	27	-	
30	40	2	30	-	
60	40	2	30	-	
70	50	2	95	5	CLEAR AND COLORLESS
75	50	2	100	10	C U T I
80	50	1	130(266°F)	3	CLEAR AND COLORLESS
90	50	1	129	25	
110	50	1	131	40	
135	50	1	137	55	
160	60	1	150(302°F)	60	C U T II
190	75	1	220	3	DARKER YELLOW
195	75	1	250(482°F)	5	
205	75	1	310(590°F)	-	C U T III

PRODUCT CAME OVER AT 310°C (590°F) .... 135 ml. IN FLASK ONLY A FILM LEFT

III. T 42-131 REPEAT TEST WITH THE SAME QUANTITIES

-	40	2	24	-	
60	45	2	30	-	
70	50	2	95	3	CLEAR AND COLORLESS
90	55	2	110	10	C U T I
95	55	2	130	5	CLEAR AND COLORLESS
120	55	2	150	50	
145	60	2	140	60	C U T II
160	70	2	100	3	DARKER YELLOW
190	75	2	230	5	
210	75	2	310	-	C U T III

PRODUCT CAME OVER AT 310°C (590°F.)..... 135 ml.

TABLE 180.

MODIFYING THE TPT/ZINC OCTOATE PRODUCT (WITH Al Cl_3 CATALYST)

WITH TETRA BUTYL T I N

T-40- 77

MATERIAL USED: 200 g. DISTILLATION PRODUCT FROM TETRA ISOPROPYL TITANATE 1/ 2 mole

BASIC ZINCOCTOATE 1/3 mole

WITH 0.5 g. Al Cl_3 CATALYST

60 g. TETRA BUTYL TIN IN

T -40-77

60 g. BENZENE

TIME min.	VARIAC	PRESSURE mm.	TEMPERATURE C.	VOLUME ml.	REMARKS
-	40	3.5	27	-	
10	70	3.5	37		CLEAR COLORLESS FLUID DISTILLS
40	70	3.5	39 (102°F)	50 ml.	C U T I
70	70	3.5	170		
90	70	3.5	170		CLEAR COLORLESS DISTILLATE
120	90	3.5	170(338°F)		TEMPERATURE BEGINS TO DROP
140	90	3.5	45	100 ml.	C U T II
					(HERE SOME YELLOW COLORAPPEARS
160	90	3.5	310 (590°F)		RAPID TEMPERATURE RISE
180	90	3.5	330	30	
230	90	3.5	340(644°F)	120	MOST OF THE PRODUCT CAME OVER AT 340°C. (644°F)

TOTAL YIELD ..... 148 g.

O X I D A T I O N T E S T O F T H I S M A T E R I A L

SET UP AT 200°C. (392°F) WITH 5 LITER AIR PER HOUR

T 40-82

AFTER 24 hrs. TURNED WHITISH , BUT CLEAR

AFTER 48 hrs. NO CHANGE

AFTER 72 hrs. NO CHANGE: WHITE, FAIRLY CLEAR NO VISIBLESEDIMENT

NO SEDIMENT UNDER MICROSCOPE VISCOSITY FAIR METALS AFFECTED

TO BE REPEATED

TABLE 181.

MORE MODIFICATIONS OF THE TPT/ZINCOCTOATE PRODUCT (WITH Al Cl_3 CATALYST)

WITH T E T R A n B U T Y L T I N

I. T 42-133

USED .... 180 g. PRODUCT WITH

60 g . TETRA n BUTYL TIN MIXED WELL

TIME min.	TEMPERATURE C.	VARIAC	PRESSURE mm.	VOLUME ml.	REMARKS
-	25	40	2	-	
60	95	45	2	5	CLEAR AND COLORLESS
70	115 (239°F)	45	2	10	CUT I
80	135	50	2	20	CLEAR AND COLORLESS
110	140 (284°F)	50	1	35	
145	90	50	1	55	
180	160 (320°F)	65	1	60	CUT II
200	230 (446°F)	70	1	5	DARKER YELLOW CUT III
220	3 1 0 (590°F)				

PRODUCT CAME OVER AT 3 1 0°C ..... 135 ml.
(590°F)

II. T 42- 139

USED 450 g. PRODUCT WITH

150 g . TETRA n BUTYL TIN

-	25	50	2	-	
30	28	55	2	-	
65	98	55	2	5	CLEAR AND COLORLESS
75	120 (248°F)	55	2	10	CUT I
80	130	55	2	15	CLEAR AND COLORLESS
120	135	55	2	85	
145	160 (320°F)	60	2	125	CUT II
150	220	60	2	10	DARKER YELLOW
225	305 (581°F)	70	1	75	DARK VISCOUS MATERIAL CUT III
305	3 2 0 (608°F)	70	1	PRODUCT	ABOUT 250 ml.

FLASH POINT .... 275°C . (525°E)

III. T 42- 141 USED 180 g. PRODUCT WITH

60 g .TETRA n BUTYL TIN MIXED WELL

-	25	45	2	-	
30	30	50	2	-	
60	95 (203°F)	50	2	10	CLEAR AND COLORLESS CUT I
90	125	55	2	40	CLEAR AND COLORLESS
120	130 (266°F)	55	2	50	CUT II
160	90	65	2	10	DARKER YELLOW
200	200 (392°F)	70	2	15	CUT III
220	3 0 5 (581°F)	70	2		

PRODUCT CAME OVER AT 3 0 5°C... ABOUT 135 ml.
(581°F)

TABLE 182.

NEW PREPARATION OF THE MODIFICATION OF THE TPT/ZINCOCTOATE PRODUCT (T 40 -115) HAVING Al Cl3 CATALYST WITH TETRA BUTYL TIN

T 40 - 120/121

USED .... 180 g.PRODUCT T 40-115 AND

60 g.TETRA BUTYL TIN

TIME min.	TEMPERATURE C	PRESSURE mm	VARIAC	VOLUME ml.	WEIGHT g.	REMARKS
-	28 (82°F)	1	40	-		
10	30	1	40			FLASK SHAKEN VIGOROUSLY FLASK CONTENT CLEAR
25	30	2	40	-		
60	30	1	50	-		
80	30	1	50	-		
90	30	1	50	-		
120	30	1	to 55	-		
130	30	1	to 60	-		BUBBLING IN FLASK
135	65 (149°F)	1	60	-		REFLUXING
138	140 (284°F)	1	60	30		CLEAR COLORLESS FLUID
140	145 (293°F)	1	60	40		
145	137 (278°F)	1	60	50		
148	130 (266°F)	1	65	50		
152	120	1	65	52		STILL CLEAR AND COLORLESS
156	108	1	to 70	52		ONLY DROPS COMING
160	102 (215°F)	1	70	52		FLASK FLUID QUITE CLEAR,LIGHT
					47 g. C U T I	YELLOW
165	90	1	70	-		
170	145 (293°F)	1	70	drops		
176	152	1	70	10		CLEAR, NEARLY COLORLESS
180	150	1	72	12		SLIGHTLY YELLOW
185	140	1	72	12		VERY SLIGHTLY YELLOW FLUID
195	128	1	72	15 and a few drops		
210	95	1	72	.....	14 g. C U T II	
218	105	1	72	-		
225	90	1	72	-		POT GETTING DARKER
227	85	1	72	-		
230	105	1	72			A FEW DROPS
235	85	1	72			A FEW DROPS
238	75	1	72	-		
240	65	1	80	-		
258	57	1	80	-		
265	75	1	80	-		
278	103	1	80	-		
285	130	1	82			A FEW DROPS AGAIN
290	150	1	80			A FEW DROPS
320	135	1	85			SOME SMALL CUT
340	240	1	85			
345	280	1	85			SOME PRODUCT, BUT DISCARDED
350	290	1	85	15		
355	290	1	85	25		
360	290	1	85	50		
370	300	1	85			
405	290 (554°F)	1	85	135 ml.		

TABLE 183.

MORE MODIFICATIONS OF THE TETRA ISOPROPYL TITANATE / ZINCOCTOATE ($AlCl_3$)

REACTION PRODUCT WITH T E T R A n B U T Y L T I N

I. T 42- 142 USED 210 g. PRODUCT WITH 70 g. TETRA n BUTYL TIN WELL MIXED

TIME min.	TEMPERATURE C.	VARIAC	PRESSURE mm.	VOLUME ml	REMARKS
-	25	40	2	-	
60	90	50	2	-	
70	95	50	2	15	CLEAR AND COLORLESS CUT I
90	120	50	2	10	CLEAR AND COLORLESS
130	135	50	2	45	
140	130	50	2	55	
190	120 (248°F)	50	2	70	CUT II
220	240 (464°F)	65	2	5	YELLOW MATERIAL
280	305	70			

PRODUCT CAME OVER AT 3 0 5°C..... 145 ml.

II. T 42- 144 REPEAT REACTION WITH SAME AMOUNTS

-	25	50	2	-	
60	95	50	2	5	CLEAR AND COLORLESS
65	100	50	2	10	CUT I
70	120	50	2	20	CLEAR AND COLORLESS
85	125	55	2	55	CUT II
135	150	55	2	15	CLEAR, SLIGHTLY YELLOW ORANGE
220	220	65	2	18	
280	300	65	2		CUT III
300	305				

PRODUCT CAME OVER BETWEEN 3 0 5° AND 3 1 5° C. (599°F)
(581°F) ABOUT 150 ml.

III. T 42- 146 REPEAT PREPARATION WITH 180 g. PRODUCT AND

60 g TETRA n BUTYL TIN MIXED WELL

-	25	45	2	-	
60	30	50	2	-	
70	95	50	2	5	CLEAR AND COLORLESS CUT I
80	120	50	2	10	CLEAR AND COLORLESS
120	135	50	2	40	
150	140	55	2	55	CUT II
160	90	55	2	10	SLIGHTLY ORANGE
230	240	70	2	15	
300	3 0 5	70	2		CUT III

PRODUCT CAME OVER AT 3 0 5°C..... ABOUT 135 ml.
(581°F.)

TABLE 184.

MORE STUDIES ON THE BUTYL TIN MODIFICATION

I. T 43 - 43

USED 450 g. PRODUCT MADE WITH Al Cl_3

150 g. TETRA BUTYL TIN

TIME min.	TEMPERATURE C.	VARIAC	PRESSURE mm.	VOLUME ml.	REMARKS
-	27	45	2-6	-	
15	27	45	2-6	-	
35	27	45	2-6	-	
60	145	60	2-6	125	LIGHT YELLOW
75	155	60	2-6	155	CUT I
150	230	60	2-6	15	DARK ORANGE CUT II
170	100	60	2-6	-	
190	3 2 2	70	2-6	4 0 0 ml.	LIGHT YELLOW PRODUCT

FLASH POINT ..... 275°C.... 526°F.

II. T 43 - 48

MIXED ..... 40 g. OF THE TIN MODIFICATION WITH

40 g. CERIUM OCTOATE INHIBITED SILICONE FLUID 510

ADDED SOLVENTS TO REMOVE RETAINED LOW CUT MATERIAL

40 g. BENZENE AND

40 g. ACETONE

REMOVED ALL SOLVENTS AND LOW CUTS UNDER VACUUM

III. CHARATERISTICS OF THIS MATERIAL AFTER TREATMENT II'

POUR POINT .... MINUS 6 5°F.

FLASH POINT ... 2 7 0°C.(518°F)

FLAME POINT .... 2 9 5°C.(563°F)

TABLE 185.

STUDIES ON THE TPT/ZINCOCTOATE PRODUCT REACTED WITH TETRABUTYL TIN(T40-120)

I. FOUR-BALL WEAR-TEST T 40-122

MIXTURE OF 1 part T 40-120 and

1 part INHIBITED DOW FLUID 510

RUN AT 60 °C . 20 kg. LOAD 30 MINUTES

SCAR ... 2.50
2.20
2.72
7.42

AVERAGE ... 2.47 x CALIBRATION FACTOR 0.145 .... 0.394 mm .

II. THE PRODUCT T 40- 120

FLASH POINT ..... 278 °C ... 537 °F.

FLAME POINT ..... 310 °C ... 590 °F.

III. POUR POINT TESTS

MIXTURE OF 50 parts T 40 -20 AND

50 parts INHIBITED DOW 510

POUR POINT ..... MINUS 6 0 °F.

MIXTURE OF 40 parts T 40-120 AND

60 parts INHIBITED DOW 510

POUR POINT .... MINUS 8 7 °F.

IV. INFLAMMIBILITY TEST T 40- 123

A STANDARD TRIANGLE WAS WIDENED AND A CRUCIBLE WAS SET SOLIDLY INTO THIS TRIANGLE. A CRUCIBLE COVER WAS SET WITH THE FLAT SIDE TO THE TOP OVER THIS CRUCIBLE . THE TEST FLUID WAS FILLED INTO THE FLAT COVER AND HEATED TO 200 °C. (392 °F) THEN A HOT BUNSEN BURNER WAS LOWERED AT AN ANGLE OF 60 ° TO THE SURFACE OF THE FLUID. IT TOOK MORE THAN ONE MINUTE UNTIL ANY FLAME APPEARED.

TABLE 186.

REACTING THE TPT/ZINCOCTOATE PRODUCT (WITH $TiCl_4$ CATALYST)

WITH T R I- n B U T Y L B O R A T E

T 38 - 97

USED.... 180 g. PRODUCT WITH

90 g.TRI n BUTYL BORATE $B(OC_3H_9)_3$

UPON MIXING N O HEAT IS EVOLVED BUT THE MIXTURE TURNS VERY VISCOUS AND SOME PARTS OF A WHITE PRECIPITATE ARE VISIBLE .

TIME min.	TEMPERATURE C.	VACUUM mm.	VARIAC I	VARIAC II	VOLUME ml.	WEIGHT g.	REMARKS
-	28	4	30	10	-		
57	110	4	40	10	10		
65	100	5	40	10	25		SLIGHTLY YELLOW
75	100	5	40	10	35		LOW CUT
80	98	5	40	10	45		
85	97	5	40	10	55		
105	110	4	40	10	65		
125	115	4	45	12	80		
130	116	4	45	12	90		FLASK CONTENT DARKENS
150	115	4	45	12	100		AS DISTILLATION PRO-
170	115	5	45	20	110		GRESSES
190	115	6	50	20	120		
240	110	5	65	20	130		
260	75	5	65	20	132	ml.	
						135 g.	CUT I
300	80	5	70	20	-		

HERE THE FLASK CONTENT WAS STUDIED.

IT WAS DARK BROWN IN COLOR AND SLIGHTLY MORE VISCOUS THAN THE INITIAL " PRODUCT".

ITS FLASH POINT WAS ... 270° C.(518° F)

ITS FLAME POINT WAS ... 275° C.(527° F)

TABLE 187.

REACTING THE TETRA ISOPROPYL TITANATE/ZINC OCTOATE REACTION

PRODUCT WITH TRI ISOPROPYL BORATE T 43 - 26

I. USED 10 parts ... 163 g PRODUCT MADE WITH Ti Cl_4 CATALYST

3 parts ... 49 g. TRI ISOPROPYL BORATE

NO HEAT ON MIXING

TIME min.	TEMPERATURE C.	VARIAC	PRESSURE mm.	VOLUME ml.	REMARKS
15	55 (131°F)	40	17	-	
45	65	40	17	25	CLEAR DISTILLATE
60	60	40	17	35	
75	73 (163°F)	40	3	50	
90	45	40	4	55	CUT I ..... 47 g.
140	45	50	22	-	
150	40	50	4	-	
180	35	60	4	-	POT CONTENT STILL LIQUID, DARK BROWN
240	40	60	4	-	
HEATING TAPE APPLIED					
260	155 (311°F)	65	4	-	
300	175 (347°F)	80	3	-	FUMES. POT STILL GOOD
305	315 (599°F)	90	3		CLEAR, LIGHT YELLOW FLUID COMING
310	315 - 317	90	3		LIGHT YELLOW, VERY VISCOUS FLUID I. PART OF PRODUCT TAKEN ... 114 g.
345	323 - 327 (614°F) (620°F)	95	3		CLEAR SLIGHTLY YELLOW FLUID II. PART OF PRODUCT TAKEN : 54 g.

TOTAL PRODUCT ..... 168 g.

II. COMPARING THE REFRACTIVE INDICES AT N_D^{25}

TRI ISOPROPYL BORATE	1.3738
LOW CUT OF I.	1.3750
HIGH CUT OF I.....	1.4562
PRODUCT MADE WITH Ti Cl_4..	1.4562
WITH Al Cl_3 ..	1.4562
BENZYLALCOHOL MODIFICATION OF PRODUCT WITH $TiCl_4$:	1.4566

III. QUALITATIVE TEST OF THE HIGH CUT (PRODUCT) FOR BORON ACCORDING TO LANGE HANDBOOL p.958

TEST SOLUTION ... CH_3OH AND H_2SO_4 5:1

TEST SOLUTION ADDED TO PRODUCT AND IGNITED THE VAPOURS. THE GREEN FLAME INDICATED THE PRESENCE OF BORON

TESTS ON THIS PRODUCT CONTINUED

TABLE 187 (CONTINUED)

MORE TESTS ON THE TRI ISOPROPYL BORATE MODIFICATION OF THE TPT/ ZINC OCTOATE PRODUCT MADE WITH $TiCl_4$ IN TEST T 43-26

IV. EXPOSURE TESTS TO AN OPEN FLAME :

	CENTIGRADE				
TEMPERATURE OF FLUID REACHED BEFORE FLAME ADDED:	175° (347°F)	215° (419°F)	260 (500F)	275° (527)	300° (572F)
SECONDS OF CONTACT WITH BUNSENBURNER FLAME AT 60 DEGREE ANGLE BEFORE BURNING :	15	13	9	5	0
		SECONDS			

V. OXIDATION REDUCTION TEST

MIXTURE OF 50 g. PRODUCT T 43-26

50 g. CERIUM OCTOATE INHIBITED SILICONE FLUID 510

TEMPERATURE OF TEST ..... 200 °C. WITH AIR STREAM

TEST DURATION .....THREE DAYS

WEIGHT OF SET UP BEFORE TEST ..... 209 g.

AFTER TEST ..... 169.8 g.

WEIGHTLOSS ..... 29.2 g. or 29 %

TABLE 188.

REACTING THE TETRA ISOPROPYL TITANATE/ZINCOCTOATE REACTION PRODUCT (WITH $Al Cl_3$ CATALYST) WITH TRI ISOPROPYL BORATE

I. T 40-110

USING 150 g. PRODUCT WITH

50 g. TRI ISOPROPYL BORATE.

THE MATERIALS WERE MIXED AND HEATED AND REFLUXED UNDER REDUCED PRESSURE.

THEN THE PUMP WAS ALLOWED TO EVACUATE THE SYSTEM FOR THE DISTILLATION

TIME min.	PRESSURE MM.	TEMPERATURE C.	VARIAC	VOLUME ML.	WEIGHT g.	REMARKS
-	0.1	75	50	-		
20	0.1	75	50	45		CLEAR COLORLESS FLUID
30	0.1	63	50	60		THE FLASK SOLUTION IS ALSO STILL CLEAR
40	0.1	30	70	65		
					48.6 g.	C U T I
70	0.1	100	70	-		
80	0.1	180	70	5		
90	0.1	200	70	5		C U T II
110	0.1	275	70			CLEAR VERY VISCOUS GOLDEN LIQUID APPEARS
130	0.1	275 - 280	70	150 ml.		DISTILLS AT CONSTANT TEMP.

II. FLASH POINT OF THIS PRODUCT ..... 290°C..... 554°F.

FLAME POINT OF THIS PRODUCT ..... 325°C..... 617°F.

III. QUALITATIVE TEST FOR BORON ON THE PRODUCT OF I. (HANDBOOK CHEM.& PHYS. p.958)

REAGENT SOLUTION : 5 : 1 VOLUME SOLUTION OF METHANOL AND H_2SO_4

MIXED EQUAL AMOUNTS OF SAMPLE AND OF REAGENT.

VAPORIZED SOLUTION BY HEATING AND IGNITED THE VAPOURS

TRI ISOPROPYL BORATE BURNS WITH GREEN FLAME

PRODUCT OF TPT/ZINCOCTOATE (WITH Al Cl3 CATALYST) BURNS WITH BLUE FLAME WITHOUT ANY TRACE OF GREEN

THE PRODUCT T 40 -110 (I ABOVE) BURNS WITH BLUE FLAME WITH GREEN HALO AND CHANGES TO GREEN FLAME. IT THEREFORE CONTAINS BORON

TABLE 189.

MORE PREPARATIONS OF THE TRI ISOPROPYL BORATE MODIFICATION

I. T 40-124

USED ..... 150 g. PRODUCT TPT/ZINCOCTOATE WITH Al Cl_3 CATALYST

50 g TRI ISOPROPYL BORATE

TIME min.	VARIAC	TEMPERATURE C.	VOLUME ml.	PRESSURE mm.	REMARKS
-	50	30	-	0.3	
20	50	48	60	0.3	CLEAR COLORLESS FLUID
30	50	30	65	0.3	
					END OF C U T I
60	70	90	-	0.3	
140	70	280	-	0.3	PRODUCT APPEARS
150/180	70	2 9 0	1 5 0	0.3	PRODUCT DISTILLS CLEAR AND LIGHT YELLOW AT CONSTANT TEMPERATURE OF 290°C. (554°F)

FLASH POINT ..... 295°C ..... 563°F.

FLAME POINT .... 320° - 325°C ..... 608°/ 617°F.

II. T 40 -131

USED .... 600 g. PRODUCT TPT/ZINCOCTOATE WITH Al Cl_3 CATALYST
200 g. TRI ISOPROPYL BORATE

TIME min.	VARIAC I	VARIAC II	TEMPERATURE C.	VOLUME ml.	PRESSURE mm.	REMARKS
-	-	-	30	-	0.5	
20	40	40	44		0.5	
40	40	40	48	70	1	CLEAR COLORLESS
60	40	40	55	150	3	MATERIAL
80	40	40	62	200	5	
90	50	50	70	220	0.5	
120	50	50	40	230 ml.	0.5	
						C U T I .... 206 g.
150	70	70	3 1 0	-	0.5	PRODUCT APPEARS
170	70	70	315	200	0.5	CLEAR GOLDEN COLOR
190	70	70	310	450 g.	0.5	

III T 40 -133

USED ..... 288 g. PRODUCT
96 g. TRI ISOPROPYL BORATE

-	-	40	-	1	
5	40	48		1	CLEAR COLORLESS FLUID
30	40	60	80	1	APPEARS
50	40	49	120	1	C U T I
70	60	90	-	1	
100	60	3 1 0		1	PRODUCT APPEARS
160	60	310(590°F)	300	1	REACTION PRODUCT

TABLE 190.

MORE STUDIES ON THE PRODUCT MODIFICATION WITH

TRI ISOPROPYL BORATE (T 40 - 110)

I. MIXTURE OF ONE PART (31 g) T-40 -110 WITH

33 g. INHIBITED DOW FLUID 510 T 40 - 113

WAS FURTHER MIXED WITH ACETONE AND BENZENE AND WAS HEATED UP TO 190°C. (374 F)

UNDER 0.1 mm VACUUM.

WEIGHT LOSS (LOW CUT) DETERMINED : NEW WEIGHT .... 56 g.

OLD WEIGHT .... 64 g.

LOW CUT REMOVED ..... 8 g.

LEFT STANDING OVER NIGHT. NO PHASE SEPARATION, BUT A SLIGHT CLOUDINESS APPEARED.

II. OXIDATION TEST : T 40 - 114

40 g. OF THE MATERIAL PREPARED IN I (T 40- 113) WERE SUBJECTED TO OXIDATION TEST WITH METALS AT 200°C. (392°F) WITH 5 LITER AIR/HOUR.

AFTER TEST WEIGHT LOSS ..... 10 g. or 25 %

COLOR ONLY SLIGHTLY DARKER

VISCOSITY EXCELLENT

METALS UNCHANGED, ONLY COPPER SLIGHTLY DISCOLORED.

SECTION II-D.

TABLE 191.

REACTING TETRA ISOPROPYL TITANATE WITH TRI ETHYL HEXYL - TRI- MELITATE (TOTM) A DERIVATIVE OF THE MELISSIC ACID

($C_{30}H_{61}COOH$) (Duflex-TOTM, Rosett Ch.Inc.,Newark)

I. T 40- 99 USED: 150 g.TETRA ISOPROPYL TITANATE
150 g.TRI 2 ETHYL HEXYL TRI MELITATE
0.1 g $AlCl_3$

TIME min.	VARIAC	PRESSURE mm.	TEMPERATURE C.	VOLUME ml.	WEIGHT g.	REMARKS
-	50	2.5	30	-		ODOR OF ISOPROPYLALCOHOL BUT EVIDENTLY THE VAPOURS PASS INTO THE TRAP
30	50	2.5	84			VAPOURS APPEAR
38	50	2.5	94			CLEAR COLORLESS MATERIAL APPEARS AND DISTILLS AS. TEMPERATURE RISES TO 110C
80	50	2.5	110	140 ml.		FLASK CONTENT DID NOT TURN YELLOW
					160 g.	CUT I
100	70	2.5	140	-		NO MORE LOW CUT
130	70	2.5	240			A VISCOUS RED ORANGE MATERIAL APPEARS AND DESTILLS AT CONSTANT TEMPERATURE OF 250 C.
140	70	2.5	250	30		FLASK CONTENT RED
150	70	2.5	250	70		CUT II
152	70	2.5	250	-		
155	70	2.5	250	-		
170	70	2.5	250(482°F)	20		FLASK RESIDUE BROWN VERY VISCOUS

II. T 40- 100 USED 75 g.TETRA ISOPROPYL TITANATE
150 g. TRI 2 ETHYL HEXYL TRI MELITATE
0.1 g. Al Cl_3
(THIS MEANS :USING ONLY 1/2 AMOUNT OF TITANATE)

-	50	2.8	30	-		
40	50	2.8	95			CLEAR COLORLESS FLUID APPEARS
60	50	2.8	110	50		
70	50	2.8	115	80		
85	50	2.8	117	85ml.		GREENISH TINT
90	65	2.8	114	- 80 g		END OF C U T I
115	65	2.8	80	-		BROWN FLUID IN FLASK
140	65	2.8	180			YELLOW FLUID DISTLLS AT CONSTANT TEMPERATURE OF 180°C.
160	65	2.8	180(356°F.)	70 ml.		CUT II
			ONLY DECOMPOSITION PRODUCT LEFT IN FLASK			

TABLE 192.

REACTING BASIC ZINC OCTOATE WITH TETRA B E N Z Y L TITANATE

I. PREPARING A TRANSESTERIFICATION PRODUCT BETWEEN TETRA ISOPROPYL TITANATE AND B E N Z Y L ALCOHOL T 38- 71

USING .... 432 g .BENZYLALCOHOL AND 285 g.TETRA ISOPROPYL TITANATE

HEAT DEVELOPED UPON MIXING

TIME min.	TEMPERATURE C.	VARIAC	VACUUM mm.	VOLUME ml.	WEIGHT g.	REMARKS
-	26	40	ATM	-		
45	86	45		20		
50	88	50		40		
60	89	55		70		
90	88	55		170		
140	89	55		280		
150	94	55		290		
160	105	55		295		
165	115(239°F)	55		300 ml.		

216 g. ISOPROPYL ALCOHOL TAKEN OFF

II. REACTING 130 g. REACTION PRODUCT OF I. (TETRA BENZYL TITANATE) WITH 190 g. ZINC OCTOATE IN PRESENCE OF 18 g. WATER T 38-83

SINCE THE REACTION PRODUCT OF I IS AT R.T. SOLID IT HAS BEEN MOLTEN ON A HOT PLATE (AT LOW HEAT POSITION) BEFORE REACTING IT WITH ZINC OCTOATE.

TIME min.	TEMPERATURE C.	VARIAC	PRESSURE mm.	VOLUME ml.	WEIGHT g.	REMARKS
-	27	40	2-4	-		
90	105	40		10		
110	112	50		25		colorless liquid
135	115	55		70		odor of Benzylalcohol
160	115	60		105 ml	103 g.	C U T I
170	165	70		10		clear colorless
180	170	70		20		
190	145	70			20 g.	C U T II
229	230	75		5		yellow liquid CUT III
230	268	75		10		yellow liquid
243	280	75		15		yellow liquid CUT IV
250	290	75		5		
257	290	75		10		
265	290	75		15		
280	290(554°F)	75		25		THE REACTION PRODUCT

Continued from page 34.)

interest in this material at this time.

In TABLE 193 the isopropyl groups in the tetra isopropyl titanate were replaced by reacting the titanate with 2 chloroethanol, and the resulting material was then complexed with zinc octoate in the presence of water. The results were not satisfactory but it is planned to repeat this preparation without the addition of water.

In TABLE 194 the reaction product of PART I was modified with a solution of penta bromophenol in benzyl alcohol. A brown reaction product was obtained, distilling between 200°C. 392°F.) and 312°C. (593°F) at 2-4 mm. pressure. This reaction product has not yet been studied with regards to its properties.

- - -

TABLE 193.

INTRODUCING A CHLOROETHANOL INTO THE TITANATE SYSTEM

T-38 -85

I. TRANSESTERIFICATION OF TETRA ISOPROPYL TITANATE WITH 2 CHLOROETHANOL

USED: 160 g . 2-CHLOROETHANOL (2 moles)

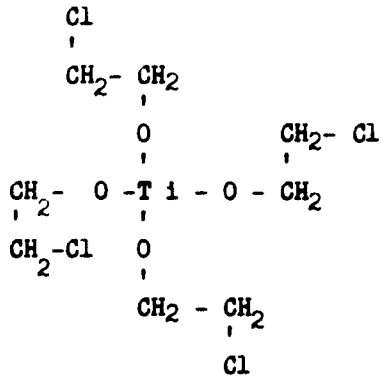
142 g TETRA ISOPROPYL TITANATE (1/2 mole)

ATMOSPHERIC DISTILLATION :

140 ml. OF ISOPROPANOL WAS TAKEN OFF IN THE COURSE OF 2 HOURS 30 MINUTES COMING OVER BETWEEN 80°AND 90 °C .

THE DISTILLATION WAS STOPPED AS SOON AS A FAINT BUT DISTINGUISHABLE ODOR OF 2 CHLOROETHANOL WAS APPARENT.

THE COLOR OF 2 CHLORO ETHYL TITANATE IS DARK BROWN. ITS FORMULA MIGHT BE SEEN AS



II. REACTING THIS PRODUCT OF I. WITH ZINCOCTOATE IN PRESENCE OF WATER T 38 - 86

USED 92 g. PRODUCT I
190 g. BASIC ZINCOCTOATE
13.5 g. WATER (3/4 mole)

ON ADDITION OF WATER A WHITE PRECIPITATE IS FORMED IN THE BROWN SOLUTION

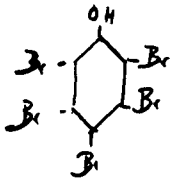
TIME min.	TEMPERATURE C.	VARIAC	PRESSURE mm.	VOLUME ml.	WEIGHT g.	REMARKS
5	38	30	2-4	5		
60	42	40		25		
120	46	50		50		CUT I
152	85	60		20		
160	90	60		30		
190	180	65		70		
210	120	70		85		CUT II
260	190	70		10		
300	190 (374F)	75		30 ml.		THE TEMPERATURE DROPPED AND FLASK CONTENT SOLIDIFIED.

(TO BE REPEATED WITHOUT WATER)

TABLE 194.

INTRODUCING BROMINE INTO THE TPT/ZINCOCTOATE REACTION PRODUCT:

FIRST INTRODUCING POWDERY P E N T A B R O M O P H E N O L INTO BENZYLALCOHOL



T 38 -99

USING 20 g PENTA BROMO PHENOL AND

100 g BENZYLALCOHOL.

THE BROMOPHENOL DISSOLVES PARTIALLY IN THE BENZYLALCOHOL AND GIVES A BROWN SOLUTION. AFTER HEATING THE MIXTURE ON A HOTPLATE, IT WAS FILTERED THROUGH GLASSWOOL.

AFTERWARDS THIS " MODIFIER" WAS MIXED WITH THE PRODUCT WHICH WAS TO BE MODIFIED:

USING .... 190 g."PRODUCT" MADE WITH Al Cl3 CATALYST

95 g." MODIFIER" PREPARED ABOVE.

THE PRODUCT DISSOLVES EASILY IN THE DARK BROWN "MODIFIER" AND THE RESULTING MIXTURE IS LESS VISCOUS THAN THE INITIAL PRODUCT.

TIME min.	TEMPERATURE C.	VARIAC I	VARIAC II	PRESSURE mm.	VOLUME ml.	WEIGHT g.	REMARKS
-	26	35	10	2-4	-		
41	75	35	10		5		CLEAR DISTILLATE COMES
63	75	35	10		25		DROP BY DROP
82	79	38	10		29		C U T I
89	104	45	12		-		
99	104	45	14		20		CLEAR, ODOR OF BENZYL-
111	104	45	15		30		ALCOHOL
150	104	55	15		40		
175	120	60	16		45		
180	160	65	16		-		CUT II
190	150	65	16		15		YELLOW LIQUID
240	120	65	20		-		
270	210	75	25		3		DARK ORANGE
330	285	75	30		5		ORANGE
350	295	75	30		13		DARK BROWN
345	298	75	30		5		
370	300	75	30		20		
380	310 (590°F)	75	30		40		BROWN PRODUCT
390	312	75	30		60		
400	310	75	30		85		
420	305 (581°F)	75	30		105		
							FLASK RESIDUE SOLIDIFIED

PART III. RESUMING WORK ON THE INTRODUCTION OF PHOSPHOR GROUPS INTO THE PRODUCT OF PART I.

INTRODUCTION

In the preceding report of this project, work was reported on the introduction of phosphorus groups into these products. This work has been continued.

SECTION A. INTRODUCING ALIPHATIC ORGANO PHOSPHATES INTO THE ALKYL TITANATES (TABLES 195-201).

The effort was made to introduce phosphate groups from tri octyl phosphate into the alkyl titanate or into the complex products of PART I. (TABLES 195-201). A reaction does take place,and products have been obtained which have interesting properties; but no definite reaction compound has been established for further evaluation. The phosphate was reacted with tetra isopropyl titanate and the resulting product further reacted with zinc octoate in the presence of aniline. Here a material was obtained (TABLE 198) which came over in distillation at 2-10 mm. Hg. pressure between 325°C. and 340°C. (617°F. and 644°F.), and which had a flame point of 326°C. (618°F.). TABLE 199 gives also satisfactory results of an hydrolytic stability test of the new material.

In TABLE 200- III an attempt is shown to further introduce a chlorine into this material by further reacting it with 2 chloroethanol; but this did not result in an increase of the flame point.

SECTION B. USING AN ALIPHATIC AND AN AROMATIC ORGANO PHOSPHATE IN THESE REACTIONS. (TABLES 202-203)

Since an interreaction between tetra isopropyl titanate and tri cresyl phosphate results in solid materials, the attempt was made to use the aliphatic tri octyl phosphate and the aromatic tri cresyl phosphate together. The resulting product (TABLE 202) was then further complexed with zinc octoate. The resulting products (TABLES 202 and 203) were not desirable in that they did burn when exposed in an open flame. Further work will be undertaken on this.

(Continued on page 68.)

SECTION III-A.

TABLE 195.

ATTEMPTING TO INTRODUCE TRI OCTYL PHOSPHATE INTO TITANATE

T 38 - 90

USING : 120 g. TRI OCTYL PHOSPHATE (TOF)

60 g. TETRA ISOPROPYL TITANATE

2 drops $TiCl_4$

TIME min.	TEMPERATURE C.	VARIAC	PRESSURE mm.	VOLUME ml.	WEIGHT g.	REMARKS
-	26	40	4 mm.	-		
40	105	50		20		
48	104	50		30		YELLOW LIQUID WHICH
53	103	50		40		
56	102	50		50		SMOKES ON EXPOSURE
70	95	60		55		
90	100	60		60		TO AIR :HYDROLYZES
110	106	65		70		
120	108(226°F)	65		75 ml.		READILY.
					61 g	CUT I
140	205(401°F)	65	4 mm.	2		
150	215	70		10		VERY STEADY CONSTANT
170	215	70		15		
180	215	70		25		DISTILLATION OF CLEAR
187	215	70		40		
205	215	70		60		COLORLESS LIQUID .
210	215	70		70		FLASK MATERIAL TURNS GRA-
220	215	70		100		DUALLY , DARK BROWN
228	215(419°F)	70		120 ml.		
					102 g.	CUT II

COMPARING THE REFRACTIVE INDEX OF TRI OCTYL PHOSPHATE (TOF)

WITH THE REFRACTIVE INDEX OF CUT II

TRI OCTYL PHOSPHATE R.I. 25°C..... 1.4405

CUT II ..... R.I. 25°C..... 1.4406

TABLE 196.

REACTING TETRA OCTYL TITANATE WITH TRI OCTYL PHOSPHATE

I. T 43 - 15

USED 120 g. TRI OCTYL PHOSPHATE (TOF)

60 g. TETRA 2 ETHYL HEXYL TITANATE (TETRA OCTYL TITANATE)

3 - 4 DROPS OF $TiCl_4$

DISTILLED USING A CAPILLARY

TIME min.	TEMPERATURE C.	VARIAC	PRESSURE mm.	VOLUME ml.	REMARKS
15	32	40	10	-	
60	32	40	10	-	
65	87	50	12		CLEAR COLORLESS LIQUID
75	85	50	12	10	
105	75	60	10	20	
135	160	60	12	-	
150	235(455°F)	60	12	5	CLEAR COLORLESS
CAPILLARY REMOVED					
180	190(374°F)	60	2	20	PRODUCT CLEAR,SLIGHTLY YELLOW
195	197	60	2	60	
200	197	60	2	85	
210	203	60	2	110	
215	203(397°)	60	2	120	P R O D U C T A
240	230 - 240 (446°F-464°F)	80	2	25	HIGH VISCOUS DARK YELLOW P R O D U C T B

PRODUCT B FLAMES AT 70°C. (158°F)

II. T 43 - 17

REACTING THE PRODUCT OF I WITH ZINC OCTOATE

USED 58 g. PRODUCT A (T 43- 15) AND
58 g. ZINCOCTOATE (18%)

			N.. O	HEAT ON MIXING. USED A CAPILLARY	
-	25	40	3	-	
15	40	40	3	15 ml.	CLEAR COLORLESS
				C U T I	
45	60	40	3	-	
65	125	40	3	10 ml.	CLEAR COLORLESS LIQUID
80	135	50	3	25	
105	100	50	3	25	
				C U T II	
110	125(257°F)	50	3	20	YELLOW DISTILLATE,FUMING
				C U T III	

NO DISTILLATE COMING OVER AND POT CONTENT SOLIDIFIED.

TABLE 197.

MORE STUDIES WITH TRI OCTYL PHOSPHATE

I. USED 80 g. TETRA ISOPROPYL TITANATE T 40 - 106

160 g. TRI OCTYL PHOSPHATE

0.2 g. $AlCl_3$

TIME min.	PRESSURE mm.	VARIAC	TEMPERATURE C.	VOLUME ml.	REMARKS
-	2.8	60	27	-	
40	2.8	60	94	-	VAPOURS APPEAR
60	2.8	60	96	-	CLEAR LIGHT YELLOW LIQUID COMES
80	2.6	60	96	100	CUT I
100	1	60	185	-	CLEAR COLORLESS DISTILLATE COMES
150	1	60	185 (365°F)	150	CUT II FLASK ALMOST EMPTY

II. USED 80 g. TETRA ISOPROPYL TITANATE

160 g. TRI OCTYL PHOSPHATE

0.5 g. $AlCl_3$ T 42- 116

TIME min.	TEMPERATURE C.	VARIAC	PRESSURE mm.	VOLUME ml.	REMARKS
-	25	30	5	-	
45	35	40	8	-	
60	90 (194°F)	40	8	-	
70	120	40	8	10	CLEAR DISTILLATE
95	125	40	5	25	
105	125	40	5	30	
120	130	40	5	50	
130	130	40	5	70	
150	130	40	4	80	C U T I
170	205	50	2	2	
190	210 (410°F)	50	2	25	CLEAR DISTILLATE
200	215	50	2	35	
210	215	55	2	50	
220	215	55	2	65	
240	215	55	2	80	
250	215	55	2	90	
260	215 (419°F)	55	2	100	
270	220	55	2	120	
280	220	55	2	130	
285	225 (437°F)	55	2	140	ml. C U T II T 42 -116

THIS CUT WAS USED FOR FURTHER REACTION

WITH ZINC OCTOATE A N D ANILINE.

TABLE 198.

ADDITIONAL STUDIES WITH TRI OCTYL PHOSPHATE

I. T 42- 118 USED 60 g. TETRA ISOPROPYL TITANATE
180 g. TRI OCTYL PHOSPHATE
0.5 g. $AlCl_3$

TIME min.	TEMPERATURE C.	VARIAC	PRESSURE mm.	VOLUME ml.	REMARKS
-	25 (77°F)	35	2-10	-	
25	25	40	2-10	-	
45	50	45	2-10	10	CLEAR COLORLESS
70	120	45	2-10	25	
90	150	45	2-10	40	
100	150	45	2-10	55	
120	150 (302°F)	45	2-10	70	
150	155	45	2-10	80	C U T I
180	200 (392°F)	45	2-10	10	CLEAR DISTILLATE
200	205	45	2-10	35	
210	215	45	2-10	65	
220	215 (419°F)	45	2-10	100	
230	220	45	2-10	120	
240	220	45	2-10	135	
250	215	45	2-10	145 ml.	C U T II T 42-118

II. T 42-117
REACTING 100 g. CUT II OF T 42-116
450 g. ZINC OCTOATE AND
50 g. ANILINE

-	25	35	2-10	-	HEAT EVOLVED UPON MIXING
60	55	55	2-10	-	
70	100	60	2-10		one drop
90	110	55	2-10	10	CLEAR COLORLESS DISTILLATE
100	115	55	2-10	20	
110	115	55	2-10	45	
120	120	55	2-10	65	
125	125 (257°F)	55	2-10	85	
135	135	55	2-10	105	C U T I
145	145 (293°F)	55	2-10	25	CLEAR COLORLESS DISTILLATE
150	145	55	2-10	35	
160	165 (329°F)	55	2-10	50	
170	215	55	2-10	70	
175	215 (419°F)	60	2-10	80	
185	230	60	2-10	120	
187	233	60	2-10	145	
190	200	60	2-10	180	
195	180	60	2-10	220	C U T II
220	185	75	2-10	5	A DEEPER YELLOW DISTILLATE
240	270 (518°F)	75	2-10	15	CUT III
280	320 - 335 (608°F-635°F)	75	2-10		PRODUCT COMING OVER DARKER IN COLOR THAN REGULAR PRODUCT BUT LOWER IN VISCOSITY

(TABLE CONTINUED)

TABLE 198. (CONTINUED)

ADDITIONAL STUDIES WITH TRI OCTYL PHOSPHATE(CONTINUED)

III. T 42- 119

USING 100 g. CUT II OF T 42 -118
450 g. ZINC OCTOATE 18%
50 g. ANILINE

TIME min.	TEMPERATURE C.	VARIAC	HEAT ON MIXING PRESSURE mm.	VOLUME ml.	REMARKS
-	28	35	2-10	-	
70	45	50	2-10	-	
90	105	55	2-10		A FEW DROPS
100	115	55	2-10	20	
110	118	55	2-10	25	
120	120	55	2-10	35	
130	120	55	2-10	55	
140	128	55	2-10	75	
150	130 (266°F)	55	2-10	100	
160	130	55	2-10	110	
170	145	55	2-10	120	
180	155 (311°F)	55	2-10	145 ml.	CUT I
190	200	55	2-10	10	
210	220	55	2-10	35	
220	225	60	2-10	55	
230	230 (446°F)	60	2-10	75	
240	230	60	2-10	100	
260	185	60	2-10	145	
265	240 (464°F)	65	2-10	180	
270	260	65	2-10	210	
280	275 (527°F)	65	2-10	220	CUT II

P R O D U C T CAME OVER BETWEEN 325° (617°F) AND 340°C. (644°F)

IV. CHARACTERISTICS OF THE PRODUCT OF III

FLASH POINT ..... 292°C. 557°F.

FLAME POINT ..... 326°C .. 618°F.

OXIDATION TEST ... USING 22.4 g. PRODUCT T 42-119 WITH METALS (Cu Al STEEL) AT 200°C (392°F) . THREE DAYS .... DARK IN COLOR. ONLY SLIGHT SEDIMENT ON BOTTOM T 42- 121

V. BENZYLALCOHOL MODIFICATION OF T 42-119

MADE USING 100 g. T 42-119 WITH 90 g. BENZYLALCOHOL (T 42-120)

TAKING OFF 60 ml. LOW CUT AT 100°C (2-10 mm PRESSURE) AND
20 ml. YELLOW CUT AT 130°C. (2-10 mm PRESSURE)

VI. BENZYLALCOHOL MODIFICATION OF T -42- 117 USING 72 g. T -42-117 AND 25 g. BENZYLALCOHOL

TAKING OFF 30 ml LOW CUT AT 88°C. AND TAKING THE DARK BROWN FLUID FROM THE FLASK : FLASH POINT : 270°C .... 518°F.
FLAME POINT : 305°C .... 580°F.

TABLE 199.

REACTING TETRA ISOPROPYL TITANATE WITH TRI OCTYL PHOSPHATE

IN PRESENCE OF A SMALL AMOUNT OF Al Cl_3

T 38 -102

USED: 60 g.TETRA ISOPROPYL TITANATE

180 g. TRI OCTYL PHOSPHATE

0.5 g. Al Cl_3

TIME min.	TEMPERATURE C.	PRESSURE mm.	VARIAC	VOLUME ml.	REMARKS
-	26	2-4	40	-	
35	30		45	-	
50	95 (203°F)		45	10	
58	95		45	20	
90	95		50	30	CLEAR ALMOST COLORLESS LIQUID
105	100		50	40	
120	95		50	60	
					CUT I
130	120(248°F)	2-4	50	5	
145	145(293°F)		60	10	
					CUT II
160	195(383°F)	2-4	60	10	
170	198		60	20	CLEAR LIQUID
180	196		60	40	
192	195		60	60	
216	195		60	90	
223	196		60	100	

100 g.OF THIS MATERIAL WERE MIXED WITH
450 g.ZINC OCTOATE AND
50 g. ANILIN AND WERE DISTILLED IN VACUUM.

NEW PRODUCT OBTAINED AT 310°C (590°F) .(T 42-123)

HYDROLYTIC STABILITY TEST OF THIS NEW PRODUCT T 42-123

T 38 - 100

USED 75 g.OF THE PRODUCT WITH 25 g.WATER AND

1.1308 g. COPPERSTRIP (SANDED AND WASHED WITH BENZENE AND ACETONE)

AFTER 72 HOUR TEST THE FLUID IS DARKER, BUT TWO PHASES CLEARLY SEPARATE. THE COPPER STRIP APPEARS IN GOOD CONDITION. WEIGHT : 1.1303 g.

WEIGHTLOSS .... 0.0005 g.

TABLE 200.

REACTING TOGETHER TETRA ISOPROPYL TITANATE, TRI OCTYL PHOSPHATE

ANILINE AND ZINC OCTOATE

I. T 42 - 124

USED: 50 g. TETRA ISOPROPYL TITANATE
50 g. TRI OCTYL PHOSPHATE
50 g. ANILINE
450 g ZINC OCTOATE

TIME min.	TEMPERATURE C.	VARIAC	PRESSURE mm.	VOLUME ml.	HEAT ON MIXING REMARKS
-	25	45	2-10	-	
35	29	45	2-10	-	
90	45 (113°F)	45	2-10	20	CLEAR DISTILLATE
110	50	50	2-10	45	
120	50	50	2-10	75	
140	55	50	2-10	95	
155	55	50	2-10	125	
160	65	50	2-10	145	
					CUT I
180	140(284°F)	50	2-10	15	YELLOW DISTILLATE
190	145	55	2-10	35	
					CUT II
	315(599°F)	70	2-10	100	DARK YELLOW
	370 - 380 (698°F.- 716°F)	70	2-10	100	DARK ORANGE, VERY VISCOUS

II. T 42 -125 BENZYLALCOHOL MODIFICATION OF I.

USED 140 g. PRODUCT T 42- 124

160 g. BENZYLALCOHOL

-	25	40	2-10	-	
30	35	40	2-10	-	
60	95	40	2-10	10	CLEAR COLORLESS
70	120	40	2-10	35	
80	125	40	2-10	50	
110	120	45	2-10	70	
120	120	45	2-10	120	
140	130	45	2-10	160	
					CUT I
160	145	45	2-10	20	YELLOW MATERIAL
200	235	45	2-10	20	
					CUT II

PRODUCT CAME OVER BETWEEN 340° AND 350°C. (644°F. AND 662°F.)

III. T 42- 125 REACTING THE PRODUCT T 42- 124 WITH 2 CHLORO ETHANOL

USED 100 g. EACH

-	25	30	2-10	-	
20	40	30	2-10	10	LIGHT YELLOW CLEAR
90	50	30	2-10	60	
140	55	40	2-10	95	DARKER YELLOW CLEAR
220	205	55	2-10	110	CUT I
240	300 - 305 (572°F.-581°F)	65	2-10		PRODUCT VERY DARK IN COLOR FLASH POINT : 260°C (500°F) FLAME POINT:264°C.(507°F)

TABLE 201.

REACTING TRI OCTYL PHOSPHATE AND ANILINE WITH TETRA ISOPROPYL TITANATE AND ZINC OCTOATE IN A S I N G L E REACTION.

T 42- 128

USED 90 g. TRI OCTYL PHOSPHATE

30 g. TETRA ISOPROPYL TITANATE

60 g. ANILINE AND

540 g ZINC OCTOATE 18 %

TIME min.	TEMPERATURE C.	VARIAC	PRESSURE mm.	VOLUME ml.	REMARKS
-	25	45	2-10	-	
20	50	45	2-10	1	
30	70(158°F)	45	2-10	26	CLEAR COLORLESS
45	75	45	2-10	86	
90	80	55	2-10	110	
110	104(219°F)	55	2-10	135	
130	150	55	2-10	175	SLIGHTLY YELLOW BUT CLEAR
150	160(320°F)	60	2-10	200 ml.	
					C U T I
160	190(374°F)	60	2-10	35	YELLOW AND CLEAR
170	200(392°F)	60	2-10	55	
175	206	60	2-10	95	
240	240	60	2-10	155	MUCH FUMES
250	240(464°F)	60	2-10	180	
					C U T II

PRODUCT CAME OVER BETWEEN 310° (590°F.) AND 312° (593°F) C.

Y I E L D ..... 1 5 0 ml.

SECTION III-B.

TABLE 202.

REACTING TETRA ISOPROPYL TITANATE WITH TRI OCTYLPHOSPHATE A N D TRI CRESYL PHOSPHATE

I. T 42- 114 USING ... 180 g. TETRA ISOPROPYL TITANATE
180 g. TRI OCTYL PHOSPHATE
180 g. TRI CRESYL PHOSPHATE N O HEAT ON MIXING

TIME min.	TEMPERATURE C.	VARIAC	PRESSURE mm.	VOLUME ml.	REMARKS
-	30	35	2-10	-	
60	80	45	2-10	-	
90	120	40	2-10	10	CLEAR YELLOW DISTILLATE
120	140	45	2-10	40	
160	140	45	2-10	80	
220	140(284°F)	45	2-10	130	
240	160(320°F)	45	2-10	170	DARKER MATERIAL COMING OVER, SEPARATED
260	150(302°F)	45	2-10	200 ml.	T 42-114 USED FOR REACTION WITH ZINC OCTOATE

II. T 42- 115 USING 191 g. DISTILLATE I
191 g. ZINCOCTOATE 18% HEAT AND COLOR CHANGE ON MIXING

-	25	35	4	-	
30	45	45	4	10	CLEAR AND COLORLESS
40	65	45	4	20	
80	80	45	4	30	
100	95(203°F)	45	4	50	
110	95	45	4	65	
120	110(230°F)	45	4	90	
125	115(239°F)	45	4	100	
130	120(248°F)	45	4	110	C U T I
140	130(266°F)	45	4	20	YELLOW DISTILLATE
150	135(275°F)	45	4	30	
160	145	45	4	55	
170	145(293°F)	45	4	75	
200	150(302°F)	45	4	100	
220	140	45	4	120	
240	140(284°F)	45	4	135	
260	135(275°F)	45	4	145	C U T II
280	150	55	4	10	DARK RED DISTILLATE
300	180	60	4	20	
310	260	70	4	30	C U T II
320	305°/310° (581°F/590°F)	70	4	ABOUT 150/175 ml.	PRODUCT

THIS PRODUCT IS LOWER IN VISCOSITY, BUT DARKER THAN REGULAR TPT/ZINCOCTOATE PRODUCT

TABLE 203.

REACTING TETRAISOPROPYL TITANATE WITH ONE ALIPHATIC A N D ONE AROMATIC ORGANOPHOSPHATE

T-38 - 89 AND 91

I. USED .... TRI OCTYL PHOSPHATE (TOF) ..... 62 g. (1/6 mole)

TRI CRESYL PHOSPHATE (TCF) ..... 61 g.

TETRA ISOPROPYL TITANATE (TPT)... 95 g.(1/3 mole)

TRACE OF Al Cl_3

NO HEAT EVOLVED ON MIXING:

TIME min.	TEMPERATURE C.	VARIAC	PRESSURE mm.	VOLUME ml.	WEIGHT g.	REMARKS
-	29	40	2-4	-		
40	35 (95°F)	40		-		MIXTURE TURNS TO DARK YELLOW, THEN GRADUALLY TO RED.
65	115	45	4	20		
80	115 (239°F)	45	4	35		
95	121	45	4	55		
120	120	45	4	75		YELLOW LIQUID
135	120 (248°F)	45	4	85		

CUT I

RED RESIDUE LEFT IN FLASK AS A SOLID.

THIS RESIDUE BURNS IN AN OPEN FLAME READILY.

II. REPEATING WITHOUT Al Cl_3 AND IN BENZENE SOLUTION
T 38 - 93

USED..... TOF .... 93 g. (TRI OCTYL PHOSPHATE)
TCF .... 93 g. (TRI CRESYL PHOSPHATE)
TPT ... 142 g. (TETRA ISOPROPYL TITANATE)
WITH BENZENE ... 5- g. AS SOLVENT

FIRST THE BENZENE DISTILLED OFF UNDER ATMOSPHERIC PRESSURE. VARIAC AT 50
TEMPERATURE ... 81 C. (177°F) TIME .... 75 minutes

VACUUM DISTILLATION

min.	C.	VARIAC	mm.	ml.	REMARKS
10	35	40	2-4	10	REMAINING BENZENE TAKEN OFF
18	108 (226°F)	40		5	
25	120	50		10	
40	129 (264°F)	50		75	YELLOW LIQUID
70	140	50		100	
80	155 (311°F)	50		130	
110	135			190 ml.	MATERIAL IN FLASK TURNS RED GRADUALLY. ON COOLING SOLID BURNS BRIGHTLY IN OPEN FLAME

(Continued from page 57.)

SECTION C. ATTEMPTS WITH OTHER ORGANO PHOSPHATES. (TABLES 204-206).

1. The attempt was made to increase the non burning characteristics by introducing a chlorine group together with the phosphates , such as reacting tetra isopropyl titanate with a tris-B-chloroethyl phosphate; but the results were not satisfactory as yet. (TABLE 204).

2. In TABLE 205 a tri butoxy ethyl phosphate was used with tetra isopropyl titanate. No high cut material was obtained, but the flask content turned into a material which appeared to have some self-extinguishing properties. In a subsequent study in TABLE 206, the self-extinguishing properties were further traced to the flask content which had remained after two cuts of lower temperature distillates had been taken off. Still further studies will be required.

SECTION D. CONTINUED WORK ON REACTION BETWEEN TITANATES AND DI 2 ETHYL HEXYL PHOSPHORIC ACID. (TABLES 207-208).

In TABLE 207 the 2 ethyl hexyl phosphoric acid is reacted with tetra isopropyl titanate, and a very viscous material is formed. When this reaction product was further reacted with zinc octoate and aniline a high cut distillate was obtained which came over at 2-10 mm. hg. pressure at 310°C. - 330°C. (590°F. - 626°F.). The properties of the material are still under study.

- - - -

TABLE 204.

ATTEMPTING TO INTRODUCE TRIS B- CHLORETHYL PHOSPHATE

T 38 - 88

I. USING 200 g. TRIS B-CHLOROETHYL PHOSPHATE (Cl- CH_2- CH_2 O)$_3$ PO

AND 100 g. TETRA ISOPROPYL TITANATE

WITH A TRACE OF Al Cl_3

TIME min.	TEMPERATURE C.	VARIAC	PRESSURE mm.	VOLUME ml.	WEIGHT g.	REMARKS
60	27 (80°F)	40	2-4	-		
96	132 (269°F)	40		5		
104	139	40		25		
107	143 (289°F)	40		40		
116	140	40		65		
122	140	40		75		
125	142	40		80	75 g. CUT I	CLEAR MATERIAL
140	122 (251°F)	40		20		DARK BROWN

AT THIS POINT THE MATERIAL IN THE DISTILLATION FLASK TURNED BROWN, BECAME VISCOUS AND SOLIDIFIED. THIS MATERIAL BURNS READILY IN AN OPEN FLAME.

II. T 38 - 92

REPETITION OF I ,BUT USING P_2 O_5 AS CATALYST INSTEAD OF Al Cl_3

USED THE SAME QUANTITITES AS IN I

NO HEAT EVOLVED ON MIXING.

-	25	40	4.5	-	
10	25	40	2	-	
70	100	40	4	30	CLEAR LIQUID
90	110(230°F)	40	4	60	
100	112	50	4	80	CLEAR LIQUID
110	120(248°F)	50	4	85	
120	121	50	4	90	CUT I

THE MATERIAL IN THE DISTILLATION FLASK TURNS DARK BROWN AND MORE VISCOUS

135	140(284°F)	50	5	10 ml.	YELLOW FLUID

THE FLASK CONTENT SOLIDIFIED.

TABLE 205.

REACTING TETRA ISOPROPYL TITANATE WITH

TRI BUTOXY ETHYL PHOSPHATE : T 38 - 94

USING .... 142 g. TETRA ISOPROPYL TITANATE (1/2 mole) AND

135 g TRI BUTOXY ETHYL PHOSPHATE (1/2 mole)

N O HEAT EVOLVED ON MIXING WITH TRACE OF Al Cl_3

TIME min.	TEMPERATURE C.	VARIAC	PRESSURE mm.	VOLUME ml.	WEIGHT g.	REMARKS
-	26	40	2-4	-		
60	40 (104°F)	50		-		REACTION MIXTURE TURNS DARKER GRADUALLY
133	80 (176°F)	40	2-4	15		CLEAR DISTILLATE , SLIGHTLY
150	85	40		75		YELLOWISH"SMOKES"(HYDROLYZES)
170	92(197°F)	40		120		IN CONTACT WITH AIR
180	95	40		145 ml.	.... 127 g.	C U T I
205	105	45	2-4	50		
235	110	45		75		C U T II
250	130	45	2-4	5		
260	135	50		10		
270	140(284°F)	55		20		
295	130 (266°F)	55		40 ml.		

THE MATERIAL IN THE FLASK IS SLIMY GRAY. WILL FURTHER BE STUDIED, BECAUSE IT APPEARS TO HAVE TO SOME DEGREE SELF EXTINGUISHING PROPERTIES .

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TABLE 206.

REACTING TETRA ISOPROPYL TITANATE WITH TRI BUTOXY ETHYL PHOSPHATE

T 43 - 18

USED 107 g.TETRA ISOPROPYL TITANATE

102 g.TRI BUTOXY ETHYL PHOSPHATE

SMALL AMOUNT OF $AlCl_3$

NO HEAT ON MIXING

TIME min.	TEMPERATURE C.	VARIAC	PRESSURE mm.	VOLUME ml.	REMARKS
-	25	40	5	-	
25	27 (80°F)	40	5	-	
40	100	40	4	10	CLEAR COLORLESS DISTILLATE,POT DARK ORANGE
60	100	40	4	60	
70	95 (203°F)	40	4	70	
					C U T I
	SOMETHING IN THE CONDENSER SOLIDIFIED AND DISTURBED THE DISTILLATION. CONDENSER CLEANED AND TEST RESUMED.				
120	133	50	4	10	CLEAR COLORLESS
125	147 (296°F)	50	4	15	
135	170 (338°F)	50	4	25	
	POT TEMPERATURE WAS HERE 220°C.				SAMPLE OF POT MATERIAL TAKEN
RESUMED TEST					C U T II
30	150 (302°F)	50	8	10	CLEAR COLORLESS
45	170 (338°F)	50	8	30	POT IS NOW DARK AND VISCOUS
					C U T III
	REACTION STOPPED WHEN POT MATERIAL BECAME VERY VISCOUS AND SOLIDIFIED ON COOLING				

STUDIES ON THE CUTS :

1) THE SAMPLE TAKEN FROM POT AFTER CUT II HAD COME OVER: IT WAS WASHED WITH ACETONE AND BENZENE.THE SOLVENTS WERE BOILED OFF. THE REMAINING FLUID WAS EXPOSED TO AN OPEN FLAME. AFTER 3 SECONDS A LOW CUT FLASHED OFF WITH A LIGHT BLUE SMALL FLAME. AFTER 5 SECONDS THE FLUID DEVELOPED A FLAME AND TURNED SOLID.THE FLAME EXTINGUISHED ITSELF .THE SOLID WAS IN FURTHER TESTS SELF EXTINGUISHING.

2) THE POT MATERIAL AFTER CUT III SEEMED TO BE ABLE TO GEL UNDER FURTHER HEAT EXPOSURE.

3) CUT III ITSELF BURNED WHEN EXPOSED TO A FLAME (NOT SELF EXTINGUISHING)

TABLE 207.

REACTING A DI-2 ETHYL HEXYL P H O S P H O R I C ACID

WITH TETRA ETHYL HEXYL TITANATE (TOT) WITH P_2O_5 AS CATALYST (T 43- 9)

I. USING 170 g. DI 2 ETHYL HEXYL PHOSPHORIC ACID

75 g. TETRA 2 ETHYL HEXYL TITANATE

0.2 g. P_2O_5

HEAT EVOLVED ON MIXING

TIME min.	TEMPERATURE C.	VARIAC	PRESSURE mm.	VOLUME ml.	REMARKS
-	40	40	2	-	
30	63	40	2	25 ml.	CLEAR COLORLESS
50	60 (140°F)	40	2	50 ml.	C U T I
85	95	50	2	25 ml.	CLEAR COLORLESS
95	135 (275°F)	50	2	35 ml.	
110	175 (347°F)	60	2	70 ml.	SLIGHTLY YELLOW NOW FUMING

THE POT MATERIAL TURNED BLACK AND VERY VISCOUS AND SUDDENLY FLOWED OVER INTO THE CONDENSER.

II. T 43-10 REPEAT TEST IN BENZENE SOLUTION

USING 150 g. DI 2 ETHYL HEXYL PHOSPHORIC ACID
50 g. TETRA 2 ETHYL HEXYL TITANATE TOT
50 g. BENZENE
0.2 g. P_2O_5

HEAT ON MIXING

-	33	40	2	-	
20	70	40	2	10	CLEAR COLORLESS
50	60	40	2	35	
80	95	50	2	60	
90	105 (221°F)	50	2	65	
					C U T I
110	165 (329°F)	55	2	75	LIGHT GREEN CLEAR

AGAIN A VISCOUS BLACK GEL MATERIAL DEVELOPED IN THE POT

III . T 43- 11 REPEAT TEST OF II WITH THE SAME AMOUNTS

-	35	50	ATM	-	
30	85	50	ATM	25	CLEAR COLORLESS (ASSUMED TO BE
75	85	50	ATM	50	C U T I BENZENE)
120	TO 180 (356°F)	50	ATM	50	CLEAR COLORLESS C U T II

THE POT MATERIAL IS NOW MEDIUM BROWN WITH SOME SEDIMENTATION.
ON HEATING IT WITH BENZYLALCOHOL, WHEREBY SOME OF THE ALCOHOL IS DRIVEN OFF, THE PRODUCT WAS FURTHER DILUTED WITH ETHYL ETHER. WITH PETROLETHER NOW A MATERIAL IS PRECIPITATED WHICH MIGHT BE A POLYMER, WHICH CAUSED THE GELATION IN II

TABLE 208.

MODIFICATION OF THE REACTION PRODUCT BETWEEN TETRA ISOPROPYL TITANATE AND DI 2 ETHYL HEXYL PHOSPHORIC ACID (T 42 -106) , RESUMED FROM TABLE 143 (page 60) OF THE THIRD REPORT

I. T 42- 122 REACTING 100 g. T 40 - 106 DISTILLATE WITH

50 g. ANILINE AND

450 g. ZINC OCTOATE 18%

TIME min.	TEMPERATURE C.	VARIAC	HEAT ON MIXING PRESSURE mm.	GREEN IN COLOR VOLUME ml.	REMARKS
-	29	40	8	-	
30	115 (239°F)	50	8	10	CLEAR DISTILLATE
45	118	50	2-10	25	
60	125	50	2-10	45	
90	130	50	2-10	70	
100	130 (266°F)	50	2-10	85	
110	135	50	2-10	105	
120	145	50	2-10	135	
130	145	50	2-10	145	
140	185 (365°F)	60	2-10	155	
160	220	60	2-10	225	
180	230	60	2-10	240	
200	230 (446°F)	60	2-10	290	
210	232	60	2-10	320	
240	190 (374°F)	60	2-10	325	
260	250 (482°F)	60	2-10	340	
300	310°- 325° (590°F. -617°F)	60	2-10	ABOUT 125 ml. PRODUCT	

II. T 42-123 REPEAT TEST WITH THE SAME AMOUNTS

-	29	45	2-10	-	
30	95	45	2-10	10	
45	115	45	2-10	45	
50	90	40	2-10	75	
75	130 (266°F)	40	2-10	125	
90	125	40	2-10	145	
140	135	45	2-10	180	
160	210	50	2-10	210	
200	215 (419°F)	50	2-10	310	
210	95	55	2-10	335	
220	195 (383°F)	60	2-10	340	
240	285 (545°F)	70	2-10	343	
300	310 - 330 C (590°F. - 626°F)		2-10	ABOUT 125 ml PRODUCT	

PART IV. ADDITIONAL WORK ON THE INHIBITION OF SILICONE FLUID 510-50 cps. (DOW).(TABLE 209)

Throughout the preceding reports work has been reported on the increase of the heat resistance of silicone fluid 510-50 by reacting it with cerium 2-ethyl hexanoate in the presence of DI SALICYLAL PROPYLENE DIAMINE (Copper Inhibitor DSPD 50, DuPont). It is interesting that this silicone fluid is evidently not a uniform material, but consists of various components, some of which cause a gelation of the fluid when heated at 260°C.-300°C. (500°F-572°F.) under a stream of air passing the fluid.

It is a regularly observed phenomenon that the heating of the 510 fluid with the two listed additions in the inhibition treatment produces color changes and an increased heat resistance, but it is also accompanied with a considerable loss in weight.

Since the total weight of the added cerium octoate and of the copper inhibitor amounts only to about 1.7% of the used weight of silicone fluid, this weight loss is nearly fully a weight loss from the fluid itself.

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TABLE 209.

THE INHIBITING OF THE DOW FLUID 510

I. NEW PREPARATION OF THE CERIUM 2 ETHYL HEXANOATE T 40 - 117

34.6 g. 2 ETHYL HEXANOIC ACID WAS DISSOLVED IN

WATER AND ETHANOL.

IT WAS NEUTRALIZED WITH NaOH TO PHENOLPHTHALEIN ENDPOINT.

21.92 g. CERIC AMMONIUM NITRATE WERE DISSOLVED IN ETHANOL.

THE SOLUTIONS WERE MIXED AND A YELLOW GREEN SOLID PRECIPITATED.

THE PRECIPITATION WAS COLLECTED BY FILTRATION AND WAS WASHED WITH

WATER AND ALCOHOL.

IT WAS DISSOLVED IN ETHYL ETHER AND FILTERED. THEN THE ETHER WAS

AGAIN EVAPORATED.

II. PREPARATION OF THE INHIBITED FLUID 510

MATERIAL 1200 g. DOW FLUID 510

2.4 g. 2 ETHYL HEXANOATE CERIUM SALT OF I

17.2 g. COPPER INHIBITOR DU PONT 65

SET UP AT 285°C (545°F) WITH ABOUT 40 liters AIR / HOUR. RUN FOR 1 2 0 HOURS UNTIL COLOR CHANGED FROM RED TO LIGHT BROWN. FILTERED THROUGH MOLECULAR SIEVE USING ACETONE AS DILUENT

ACETONE EVAPORATED

WEIGHT RECOVERY .... 900 g.

WEIGHT LOSS ..... 2 5 %

III. REPEAT TESTS

	T 43-34	T 43-36
CERIUM SALT	1.6 g.	1.6 g.
COPPER INHIBITOR:	12.8 g.	12.8 g.
FLUID	800 g.	805.5 g.
TEST DURATION	72 hrs.	112 hrs.
TEMPERATURE ..	275 - 290°C (527°F-554°F)	280°C. (536°F)
FILTER THROUGH PAPER	CLEAR GOLDEN	CLOUDY
WEIGHT LOSS	2 3 %	20 %

WORK SCHEDULED FOR THE NEXT REPORT PERIOD.

The work in the next report period is scheduled to include the following aspects:

1. Preparation of a larger amount of the tetra butyl tin modification of the reaction product between tetra isopropyl titanate and basic zinc octoate.
2. Preparation of a larger amount of the corresponding modification with tri isopropyl borate.
3. Evaluation tests on both these materials.
4. Further study of the reactions between tetra alkyl titanates and tin organics, using, for instance, di-n-butyl tin dimethoxide, tri-n-butyl tin 2-ethylhexanoate, hexabutyl di tin, or similar compounds.
5. Continuation of the study of certain of the phosphate derivatives from Part III of this report.
6. Efforts to introduce molybdenum organic groups in these titanates.
7. Further studies on the relationship between high viscous fluids of good lubricity with low viscous diluents of poor lubricity in four-ball wear-tests at varying temperatures and weight loads.

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